

TEMP #
162236

NG4-16268

SECOND QUARTERLY REPORT

6th Reporting Period

19 August 1963

to

19 November 1963

NASA CR-55743

DEVELOPMENT OF HIGH ENERGY
DENSITY PRIMARY BATTERIES
200 Watt Hours Per Pound of
Total Battery Weight Minimum

Contract Number: NAS 3-2775

LIVINGSTON ELECTRONIC CORPORATION

Montgomeryville, Pennsylvania

Telephone: 215 OXbow 9-3585

by

W. F. Meyers
(Principal Investigator)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Lewis Research Center

Auxiliary Power Generation Office

Cleveland, Ohio

Technical Manager, Mr. W. A. Robertson, 86-1

December 30, 1963

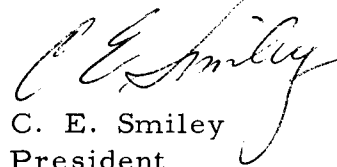
Mr. John J. Fackler, Contracting Officer
National Aeronautics and Space Administration
Space Power Systems Procurement Section
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio, 44135

RE: Contract No. NAS3-2775

Dear Mr. Fackler:

We are enclosing the Second Quarterly Report revised and delivered in accordance with instructions received from your staff.

Yours very truly,



C. E. Smiley
President
Livingston Electronic Corporation

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ERRATA

Page 33

Delete entries for
"Propylene Carbonate + Tetramethyl Ammonium Chloride + SO₂(g)."

-TABLE OF CONTENTS-

	<u>Page No.</u>
INTRODUCTION	1
QUANTITATIVE DESCRIPTION OF PROGRESS	2
<u>Part</u>	
I. SOLVENT ORIENTED BATTERY EQUATION	4
II. ANALYSIS OF SPECIFIC RESISTANCE AND TAFEL CONSTANT DATA	17
III. THEORETICAL APPROACH TO ANODES.	56
IV. BATTERY CONSTRUCTION AND TESTING.	58
V. RESEARCH CELL AND SEPARATOR RESISTANCE MEASUREMENT EQUIPMENT	60
VI. MATERIALS TESTING.	66
VII. WORK TO BE PERFORMED.	71
REFERENCE I	76
REFERENCE II	81
REFERENCE III	82
APPENDIX I	86
APPENDIX II	89
APPENDIX III	92

-LIST OF FIGURES, TABLES, AND PLATES-

			<u>Page No.</u>
PLATE	I	Glass "U" Tube Cell	8
TABLE	I	Results of Aqueous Test Cell	9
FIGURE	I	Electrolyte C, D, and R Values	16
FIGURE	II	Conductivity Test Cell	19
FIGURE	III	Physical Model for Solvent Oriented Battery Energy Equation.	20
FIGURE	IV	Strip Chart	21
FIGURE	V	Schematic of Automatic Recorder	22
FIGURE	VI	Plot of X vs Log J.	24
TABLE	II	Specific Resistance and Tafel Data	25
GRAPHS		Specific Resistance and Tafel Data Based on Table II	37
FIGURE	VII	Schematic Diagram	63
TABLE	III	Research Cell Recorder Functions	64
FIGURE	VIII	Load Current Regulator and Chopper Schematic. . .	65
TABLE	IV	Materials Compatibility.	68
TABLE	V	Materials Compatibility.	70
PLATE	II	Lithium Bronze Anode Vehicle	73
PLATE	III	Glass Electrode Immersed in Lithium Bronze. . . .	74
PLATE	IV	Mg-Mg(OH) ₂ /KMnO ₄ Cell	75
TABLE	I	Appendix I.	87
FIGURE	I	Appendix I.	88

INTRODUCTION

The performance of a battery, while requiring electrodes, is dependent primarily upon the liquid which forms the electrolyte. This electrolyte determines which electrodes may be used. For example, an excellent negative electrode would be lithium, but a less reactive solvent than water is required. In order to achieve the heretofore unapproached goal of a 200 watt hours per pound battery, solvent orientation was decided upon; and a theoretical electrolyte equation was developed. This equation is a useful tool for selecting electrolytes for high energy density battery testing.

The theoretical studies concerning the role of the solvent in a battery have been completed, and the results are presented herewith in engineering form. Following this, the theoretical study of electrodes was started.

The concept of using atmospheres, other than air, to provide improved electrolyte conductivity has been verified by experiments.

Automatic recording of data for many electrolyte-atmosphere systems is in progress. These data are being evaluated by means of the theoretical equation concerning the solvent. The great quantities of information issuing from the recorder indicates that this method of collecting data will make the study of many new battery electrolytes practical.

QUANTITATIVE DESCRIPTION OF PROGRESS

The goal of this research program is to develop a battery of 200 watt hours per pound of total battery weight. It was decided to segregate the overall task into logically discrete segments so as to permit a methodical attack.

The first segment selected was the role of the solvent. As formidable as this role may be, the numerous inter-relationships have been resolved; and a figure of merit based upon watt hours per pound has been evolved which should be sufficiently accurate for screening useful solvents for further study. (Part I Page 4)

Methods for mass production of pertinent electrochemical data for these evaluations have been designed, constructed, and placed into operation. Initial output from the strip chart recorder monitoring this work indicates that forceful methods will be required to properly evaluate this flood of information in terms of the solvent figure of merit. Initial data has been manually treated though the coverage was necessarily sparse due to the calculation load. (Part II Page 17)

Considering the engineering compromises involved in a practical battery, it is seen that, in searching the known solvents again, a favorable area may be brought to light. Of perhaps greater importance, was the realization that most previous batteries have operated in a normal air atmosphere or under sealed conditions. The studies provided for in this assignment brought to light the interesting concept that other atmospheres are equally possible. Thus, the powerful scanning system given above will have the task of evaluating a vastly larger area composed of solvent-atmosphere combinations. Most of these possible battery combinations are totally new. (Part II Page 17)

Following characterization of the role of the solvent-atmosphere systems, a theoretical approach to electrode potentials was selected as the next segment of the overall task. While thermodynamic values may be available for aqueous reactions and free energies of dry crystalline products, the contribution of the solvent in determining realistic voltages and energy densities is frequently overlooked. Initial approaches to account for the effect of the solvent and atmosphere upon voltage and energy are presented herein.

Reaction kinetics, particularly for irreversible systems as permitted in primary batteries, comprise a third and more cumbersome theoretical segment of the overall mission. However, just as the theoretical consideration of electrode thermodynamics may be restricted to only those solvent-atmosphere systems having favorable figures of merit, the more detailed electrode kinetics need only be applied to systems satisfying the theoretical requirements of both the solvent-atmosphere and electrode thermodynamics. (Part III Page 56)

Some battery construction and testing of an investigative nature has already been started, and data is included in this report.

Considerable work has been done concerning compatibility of separators and materials of construction with solvents, solvent-atmosphere, and solvent-solute-atmosphere combinations. The additional data, since the first quarterly report, is presented herein. It is interesting to note that while many materials are compatible with many pure solvents, the addition of the atmosphere, and particularly the solute makes many materials unsatisfactory.

The literature search continues, and the results of the second quarter's readings are included in this report as References I, II, and III, pages 76, 81, and 82.

PART I

I. THE SOLVENT ORIENTED BATTERY ENERGY EQUATION

In scanning the potentially vast number of possible battery combinations for systems capable of higher energy density, it seemed desirable to separate the general problem into logically discrete segments so as to permit a methodical attack.

The first segment selected in this work was the role of the solvent. The operation of a battery might be characterized by the forceful and electronic transfer of electrons from a metal anode through an external load to a non-metal cathode. For this to occur it is required that there be a consistent internal flow of charge through the battery by other than electronic conduction. The solvent, therefore, must be capable of conducting charged ions. This may be characterized by the specific resistance of solutions prepared with this solvent. While the role of the solute in conductivity is vital, there is the general limitation that the solute must consist of the cell reaction product or other ions with fairly large electrode potentials. Conversely, those ionic solutes most resistant to displacement are not generally the most soluble. Therefore, despite the added quantity of measurements required, a number of suitable salts of medium to high resistance to decomposition must be studied in each solvent for a proper evaluation. The following have been chosen:

Aluminum chloride	Tetramethyl ammonium chloride
Magnesium sulfate	Sodium iodide
Potassium bromide	Aluminum fluoride
Lithium chloride	Potassium iodide
Lithium fluoride	

Ionic conductivity is not the only important facet of the role of the solvent in a battery. Just as the solute ions must not be displaced from solution by the anode or cathode, neither may the solvent be decomposed nor displaced to any significant degree. Unfortunately, a high dielectric

constant (due to a high dipole moment) generally leads to a low decomposition potential. This, therefore, leaves few generally useful solvents for battery use. Solvent mixtures fare worse in that they usually offer the worst features of each solvent from a decomposition standpoint.

Solvent decomposition may be characterized by the Tafel equation when a reasonable number of solutes are tested. While polarization or over-voltage depends upon the nature of the electrode surface, the evolution of H_2 on bright noble metal electrodes is generally higher than for other electrodes and depends primarily upon the solvent. A derivation of the modified Tafel equation is given in Appendix II, Page 89.

Consequently, it is concluded that the value of a solvent in a battery will depend to a significant degree upon the specific resistance and Tafel parameters defined to include not only the constant in the overvoltage function, but the practical equivalent of the theoretical decomposition potential and auto-ionization constant contribution.

A similarity in concept to the energy storage capability of an electrolytic capacitor is noted here. This capability depends upon the capacity to the first power and voltage to the second power, which may be stated as: $W = \frac{1}{2} CV^2$. The energy storage capability of an ordinary battery is not simply defined, but the effect of the solvent upon the energy maximum has been approximated herein and the relative importance of the specific resistance and decomposition potential constants characterized. The most striking result of this derivation was that the specific resistance was significant only to the extent of the function $(D \ln R)$, where D is the Tafel slope and R is the specific resistance. By contrast the Tafel constant C emerges in significance directly to the first power.

Since compromises from the true engineering viewpoint must be met in a practical battery system, a reappraisal of the field of known solvents may lead to the desired objective. Indeed, it was interesting to

note from the equation that water should be capable of sustaining a 3.2 volt battery. The automotive storage battery tops the conventional voltage list with 2.15 volts, and more recently introduced cells have lower and lower voltage. For example, the zinc/silver peroxide cell gives 1.5 volts. The problem is similar in character to the rocket engine where, it might be said, extremely high energy fuels are available; but their reaction temperatures may exceed the limits of available engine construction methods and materials. The solvent in a battery is analogous to the engine. It is the means by which the energy of the fuel (anode) and oxidizer (cathode) is utilized to produce useful work.

Since R emerges in the equation as of lesser importance than voltage, it follows that the solvent dielectric constant need not be the major design factor.

Most aqueous batteries have operated in air or under sealed conditions. One aspect of the current study has brought to light the interesting concept that other atmospheres are equally possible. This realization extends the scope of the solvent study since it differs drastically from the usual solvent pair concept in that the secondary solvent need not be present as a liquid capable of decomposition by the active electrodes. Thus, a normally gaseous, highly polar material at less than its vapor pressure, in contact with salt can promote solution and conductivity in a solvent even though such complexes are not stable under "normal" atmospheric conditions. While silver chloride cannot be considered excellent from a potential standpoint, the effect of an ammonia atmosphere upon approximate specific resistance in pyridine is shown by the following:

NH_3	Specific Resistance of Saturated Solutions
0 pounds per square inch	10^8 ohm cm.
60 pounds per square inch	10^4 ohm cm.
90 pounds per square inch	10^1 ohm cm.

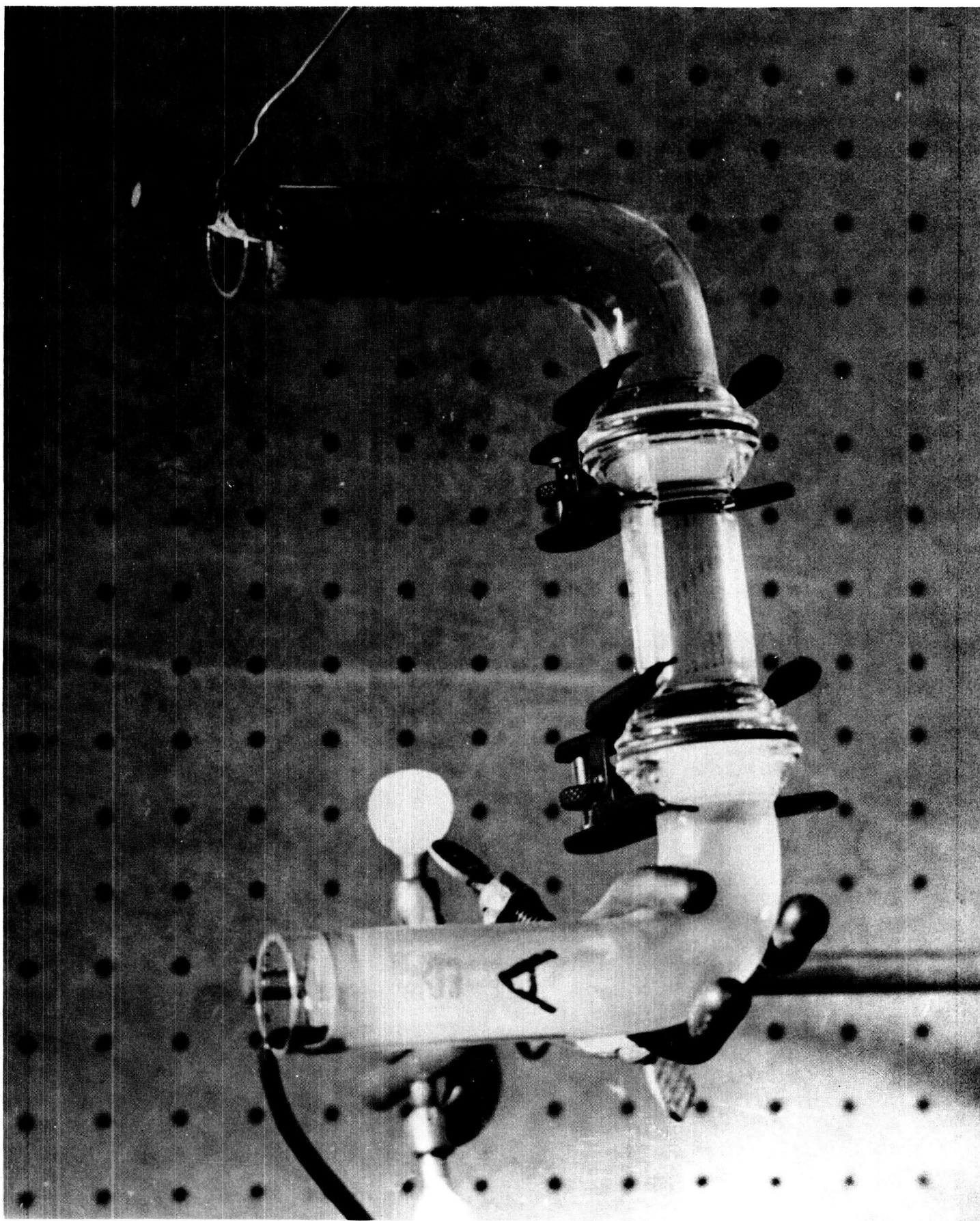
This line of reasoning is not intended to minimize the importance of the total aspect of battery technology but rather to emphasize and separate the various factors into logical groups of sufficiently few variables as to allow theoretical analysis and evolution of specific useful experiments. A specific treatment of the role of the solvent is described below.

In following periods the role of the electrodes will be examined with particular reference to solvent solute atmosphere combinations which may have favorable specific ranges of specific resistance and Tafel constants.

These equations are interesting in that they suggest specific experiments. For example, a 3.2 v. aqueous cell ($W = 400$ watt hours per pound) is clearly called for. Such battery has apparently not been reported in the literature. Inspection of the derivation of the equation to see what factors were responsible for the significant increase over the energies currently available from aqueous batteries revealed that the contribution of the auto-ionization constant has not been fully exploited. An alkaline anolyte, coupled with an acid catholyte (by means of recently available ion exchange membranes), could provide for the use of more active electrodes in aqueous cells: Using the alkaline magnesium electrolyte of Losier¹, a negative ion exchange membrane to retain the hydroxyl ion, a reaction product dump or salt bridge, a positive ion exchange membrane to isolate the catholyte, and a hypochlorous acid cathode (Plate I, Table I, pages 8 and 9) did indeed provide a stable 2.5 volt (0.3 V above the minimum value of 2.2 as required for 200 watt hours per pound).



Continuing the analysis presented in the previous quarterly report, calculus has been used to arrive at a practical result. Setting the derivative of energy with respect to discharge time equal to zero appears to be correct and gives a value for time in terms of voltage. Substitution of this function for time in the equation leads to the condition where energy is a function of the single variable, cell voltage. In the subsequent derivation this led to equality of the corrosion and electrolyte resistance loss terms.

In response to questions² concerning the definition of the term "time"



Glass "U" Tube Cell

TABLE I
RESULTS OF AQUEOUS TEST CELL

<div> <div> <div>Mg</div> <div> <div>Mg(ClO₄)₂</div> <div>+</div> <div>Mg(OH)₂</div> </div> </div> <div> <div>+</div> <div>+</div> <div>+</div> <div>+</div> </div> <div> <div>MgCl₂</div> <div> <div>-</div> <div>-</div> <div>-</div> <div>-</div> </div> </div> <div> <div>HCl</div> <div>+</div> <div>HOC1</div> </div> <div>:C</div> </div>		
Load of 2K  Elapsed Time (hr.)	Potential (load)	(Open Circuit) Potential
Start: 0:00	2.0V	2.8V
0:15	2.0	2.7
0:30	2.0	2.5
0:45	2.2	2.5
6:15	2.3	2.5
12:00	1.6	2.45
20:30	1.6	2.5
<u>Cathode Agitated</u>		
20:30	2.5	2.65
End: 23:00	2.4	2.5
<hr/>		
Same Cell Load 500 		
Start: 0:15	2.1	2.5
3:00	2.1	2.4
3:30	2.2	2.4
End: 20:00	1.8	2.5

in the equation, it was decided to shift the operating point of the equation so that the corrosion loss would be 10 times the resistance loss, thus providing for, at least, an arbitrary allocation to activated stand or shelf life. Another modification of the basis for the derivation given below was the increase of corrosion area to an arbitrary 10 times the value measured on bright platinum electrodes. This change was made to make at least some allowance for the use of electrodes of a porous nature. The arbitrary aspect of the above two restrictions is not as great as might be expected in the final analysis since it is the log of the factor 10 which becomes directly involved with the electrolyte specific resistance and Tafel constants.

¹ U. S. Patent 2,993,946

² Technical meeting at Lewis Research Center, September 18, 1963.

DERIVATION

In view of the above discussions, the equation is derived in terms of the electrolyte parameters on a basis of one pound of electrode reactants and the definition:

$$\left\{ \begin{array}{c} \text{External} \\ \text{cell energy} \end{array} \right\} = \left\{ \begin{array}{c} \text{External} \\ \text{cell voltage} \end{array} \right\} * \left\{ \begin{array}{c} \text{External} \\ \text{cell current} \end{array} \right\} * (\text{discharge time}) \quad (1)$$

DEFINITION OF TERMS

- A = Geometric electrode area
- F = Faraday's constant in English units (amp hours) per (pound equivalent weight)
- I = Theoretical current (Stoichiometric)
- J = Corrosion current density
- L = Inter-electrode spacing
- M = Equivalent weight of combined electrode reactants (lbs. per lb. -equivalent)
- Q = Theoretical capacity of reactants = $\frac{12,180}{M}$ amp. hours = F/M
- R = Electrolyte specific resistance
- T = Discharge time with arbitrary allowance for stand
- W = The maximum practical value of Y with variation in X
- \overline{W} = An approximation of W for screening purposes
- X = Couple voltage (internal)
- Y = Cell energy, watt hours per pound of electrode reactants
- C & D are modified Tafel constants measured for each electrolyte
- G approaches X by iteration
- S & H are constants

$$\text{Let: (External cell voltage)} = (X - IR \frac{L}{A})$$

The corrective term IRL/A could be more exactly stated as (I-10AJ) RL/A. However, expansion of this term in the equation indicates that 10AJ could be neglected.

Let: (External cell current) = $I - (10AJ)$

The theoretically available current is reduced by a corrosion current of 10 times the apparent cell area times the corrosion current density (See Appendix II and Page 89).

$$\text{Therefore: } Y = (X - IR \frac{L}{A}) (I - 10AJ) T \quad (2)$$

$$\text{From Appendix I: } I = \frac{Q}{T} = \frac{F}{MT} = \frac{F}{T} e^{(HE - S)}$$

$$\text{From Appendix II: } J = e^{(X-C)/D}$$

Hence:

$$Y = XIT - 10XJAT - I^2 R \frac{L}{A} T + 10IRLJT \quad (3)$$

$$= XQ - 10XJAT - \frac{Q^2}{T} R \frac{L}{A} + 10QRLJ \quad (4)$$

$$= XQ - 10XAT e^{(X-C)/D} - Q^2 \frac{RL}{AT} + 10QRL e^{(X-C)/D} \quad (5)$$

$$= \frac{XF}{M} - 10XAT e^{(X-C)/D} - \frac{F^2 RL}{M^2 AT} + 10 \frac{F}{M} RLe^{(X-C)/D} \quad (6)$$

$$Y = XFe^{(HX-S)} - 10XATe^{(X-C)/D} - F^2 \frac{RL}{AT} e^{(2HX-2S)} + \quad (7)$$

$$+ 10FRLe^{HX-S + (X-C)/D}$$

$$(\text{chemical}) = XFe^{(HX-S)} \quad (8A)$$

$$(\text{corrosion}) = 10XATe^{(X-C)/D} \quad (8B)$$

$$(\text{resistive}) = F^2 \frac{RL}{AT} e^{(2HX-2S)} \quad (8C)$$

$$(\text{loss recovery}) = 10FRLe^{HX-S + (X-C)/D} \quad (8D)$$

The (corrosion) and (resistive) loss terms are necessarily less than the chemical term. The loss recovery term is less than the loss terms. For this reason, it will be neglected in the screening process as was the correction term $10AJ$ in the cell voltage correction term.

Let: (corrosion loss) = 10 (resistive loss)

$$10XA_{Te}^{(X-C)/D} = \frac{10F^2RL}{A_{Te}(2S-2HX)} \quad (9)$$

Hence: $T = \frac{F}{A} \sqrt{\frac{RL}{X}} e^{HX-S - (X-C)/2D}$ (10)

This expression increases T and as a result, we are now operating below peak Y. This represents more practical operating conditions (peak Y occurs when $dY/dT = 0$).

Substituting this expression of T into equation (7) yields:

$$Y = XF e^{(HX-S)} - 10XF \sqrt{\frac{RL}{X}} e^{HX-S + (X-C)/2D} - FRL \sqrt{\frac{X}{RL}} e^{HX-S - (X-C)/2D} \quad (11)$$

$$Y = XF e^{(HX-S)} \left(1 - 10 \sqrt{\frac{RL}{X}} e^{(X-C)/2D} - \sqrt{\frac{RL}{X}} e^{(X-C)/2D} \right) \quad (12)$$

Hence:

$$Y = XF e^{(HX-S)} \left(1 - 11 \sqrt{\frac{RL}{X}} e^{(X-C)/2D} \right) \quad (13)$$

THE ELIMINATION OF X

An expression for X in terms of the experimental parameters is now needed. Attempts to set $dY/dX = 0$ have not as yet led to an explicit solution for X in terms of the constants R, C, and D.

However, letting:

$$U = XF e^{(HX-S)}$$

and $V = 11 \sqrt{\frac{RL}{X}} e^{(X-C)/2D}$

then $Y = U (1-V)$

The term U is continually increasing as X increases but V increases slowly at first then rises violently through unity as V becomes significant with respect to unity. Thus an approximate solution for

maximum practical Y , \bar{W} , is possible by setting V at some small fraction of unity. The term $(1-V)$ represents the electrical efficiency. A value of 75% seems reasonable though choosing 90% would effect but little change in the resulting value of X and \bar{W} , the approximate figure of merit for the solvent.

Tentatively for screening purposes, the electrolyte electrical efficiency will be set at 75% and the more exact equations (13 or 7) will be used on those electrolytes which give figures of \bar{W} approaching 200 watt hours per pound.

Hence:

$$11 \sqrt{\frac{RL}{X}} e^{(X-C)/2D} \doteq 1/4 \quad (14)$$

$$(121) (16) \frac{RL}{X} e^{(X-C)/D} \doteq 1 \quad (15)$$

$$X \doteq (121) (16) RLe^{(X-C)/D} \quad (16)$$

Taking the natural logarithm

$$\ln X \doteq \ln 1936 + \ln RL + \frac{X-C}{D} \quad (17)$$

$$X \doteq G = C - 7.57 D - D \ln RL + D \ln G \quad (18)$$

This expression can be solved by iteration:

$$\bar{W} = 3/4 GF e^{(HG-S)} \quad (19)$$

At this point, it is convenient to find a minimum G such that $\bar{W} = 200$ watt hours per pound.

$$\text{Setting: } 200 = 3/4 GF e^{(HG-S)} \quad \text{Let } B = 3/4 F = 9,135 \quad (20)$$

$$\frac{200}{B} = Ge^{(HG-S)} \quad (21)$$

In equation (21), it is desirable to remove the exponential term by expressing it in another form. This can be accomplished by means of a Taylor Series. As a result, G was found to be 2.2 volts minimum.

Hence, a necessary condition in order to obtain 200 watt hours per pound is that $X = 2.2$ volts or greater.

meant with respect to unity. Thus an approximate solution for

THE C MINIMUM EQUATION

The process for evaluating \bar{W} is too lengthy for manual use. It would be more convenient to restrict the experimental parameters such that inspection of experimental data would indicate when $\bar{W} \geq 200$ watt hours per pound. Since $X_{\text{minimum}} = 2.2$ volts: From Equation (18):

$$2.2 = C - 7.57 D - D \ln RL + D \ln 2.2 \quad (22)$$

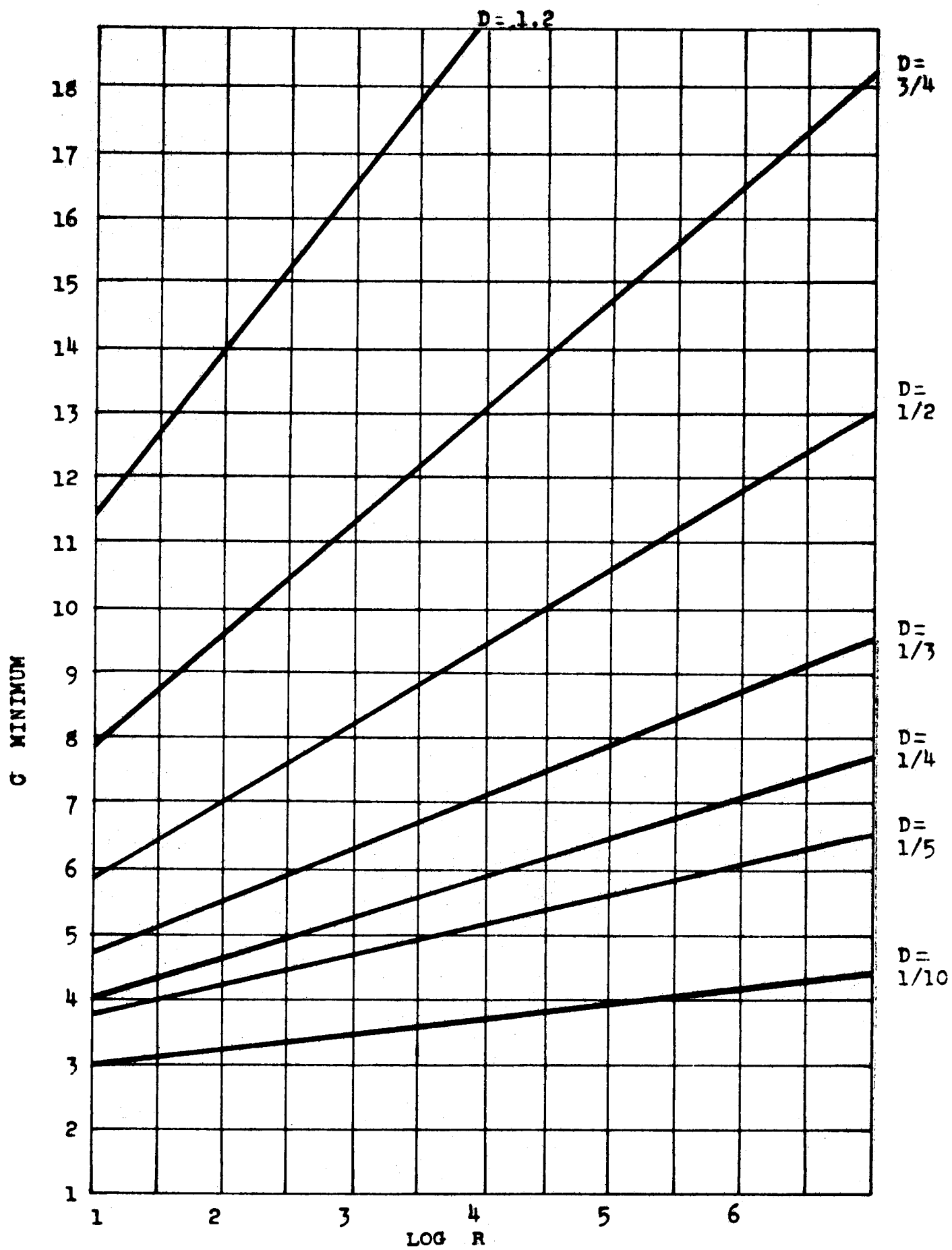
$$\therefore C_{\text{minimum}} = 2.2 + D (6.77 + \ln RL) \quad (23)$$

$$\text{or } C_{\text{minimum}} = 2.2 + D (5.06 + 2.30 \log_{10} R) \quad (24)$$

where L , the inter-electrode spacing, is set at $1/5$ cm. as a practical minimum value.

C_{minimum} is now a function of D and $\log_{10} R$. By choosing appropriate values for D and plotting C_{minimum} versus $\log_{10} R$ we obtain a family of lines (See Figure 1, Page 16) which enables one to compare C_{minimum} with $C_{\text{experimental}}$. A value of $C_{\text{experimental}}$ equal to C_{minimum} indicates 200 watt hours per pound.

The equations do not recognize that a physical limit of approximately 6 volts exists for normally available electrodes. Thus, an upper limit is also set on the values of C considered. For those electrolytes which qualify by this test, a figure of W will be determined numerically from equation (13) or (7).



ELECTROLYTE C, D, R VALUES FOR APPROXIMATELY 200 WH/lb.

FIGURE I

PART II

ANALYSIS OF SPECIFIC RESISTANCE AND TAFEL CONSTANT DATA

Provided that the coordination requirements of the conducting solute are met, the dielectric constant of the primary solvent may not need to be high. This permits the consideration of such battery electrolytes as common hydrocarbons containing an alkali halide coordinated with an atmosphere of a highly polarized compound. If the secondary solvation sheath of the ions still requires the action of a high dipole material, a small quantity of such normally solid substances as acetamide may be dissolved into the primary solvent whereupon its migration to the surfaces of the charged species provides an activity far out of proportion to the actual concentration of the secondary ligand.¹

It is, therefore, planned to measure conductivity in many primary solvents irrespective of the dielectric constant value but in the presence of unusual atmospheres such as NH_3 , SO_2 , and other polar materials substantially below their vapor pressures. When favorable conductivities have been obtained, the effects of solid polar additives may be expected to provide further conductivity increases.

In the following, Part A is a description of the method used to collect the specific resistance and Tafel constant data; and Part B is the method used to evaluate the data.

The information collected to date appears to confirm the hypothesis as stated in the first paragraph.

(A) Specific Resistance and Decomposition Potential Measurements

Specific resistance and decomposition potential data required for establishing the figure of merit, W , of solvent-solute-atmosphere systems

¹Abstract Control #4004, Livingston First Quarterly Report

as battery electrolytes are being generated on a continuous basis. The solvent and solute to be evaluated are introduced into the conductivity cells show in Figure II on page 19. At the beginning of each run, internal resistance for each of the conductivity cells is recorded at 1000 cps. Next, d.c. potentials of 1 through 10 volts are applied through the series limiting resistors and the platinum electrodes in 1 volt and 10,000 ohm steps as shown in Figure III on page 20. The maximum current is limited to 100 microamperes.

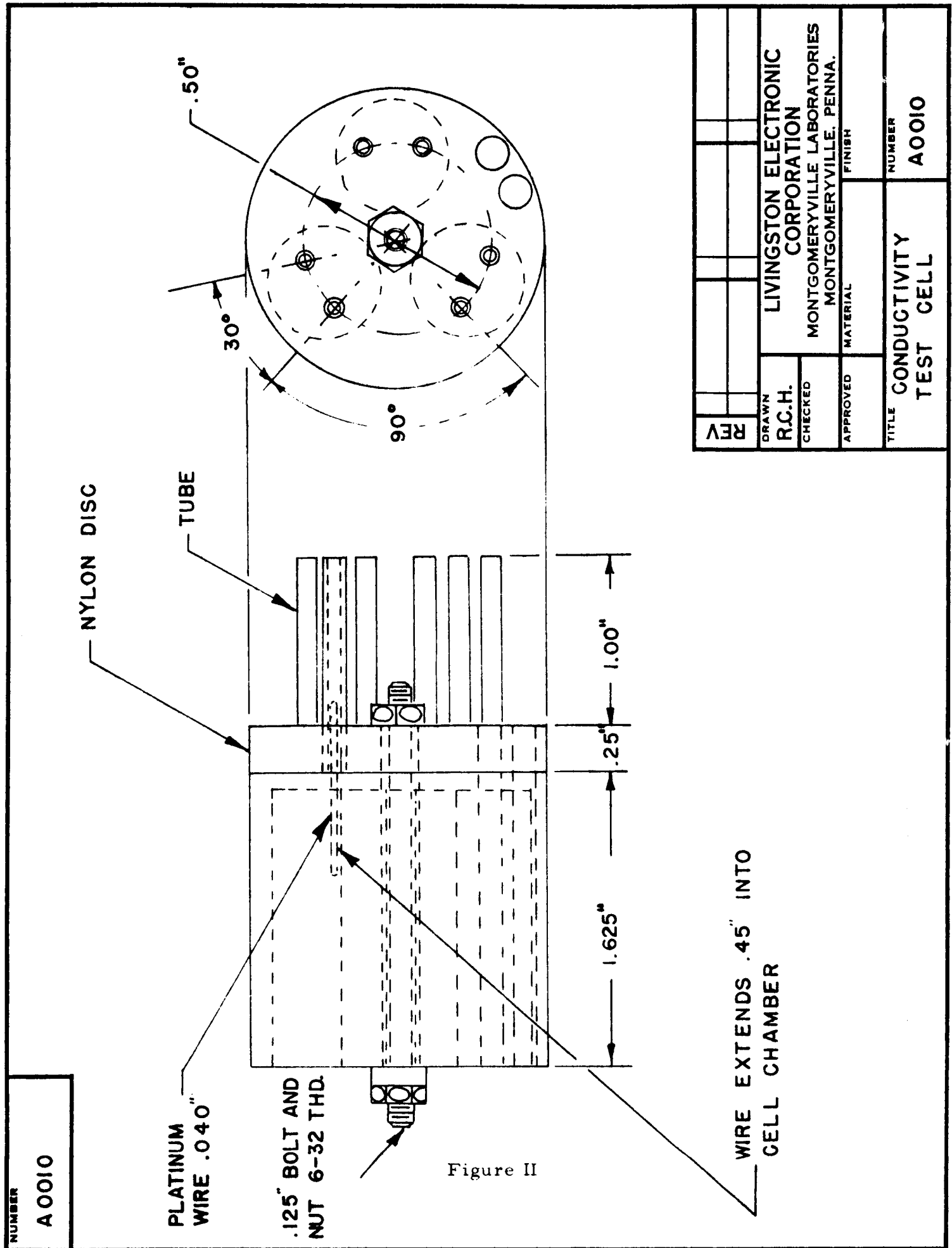
After a set of reference points at atmospheric conditions is obtained, the test chamber is purged free of air; and the ligand gas is allowed to flow gradually into the test chamber through a stainless steel capillary. The cell currents and ligand gas pressure are continuously recorded on a strip chart as show in Figure IV, page 21 by an automatic recorder (see schematic in Figure III, page 20*). The run is allowed to continue until the test chamber pressure equals the pressure of the ligand gas in the supply tank, and until steady-state conditions in the conductivity cells are indicated.

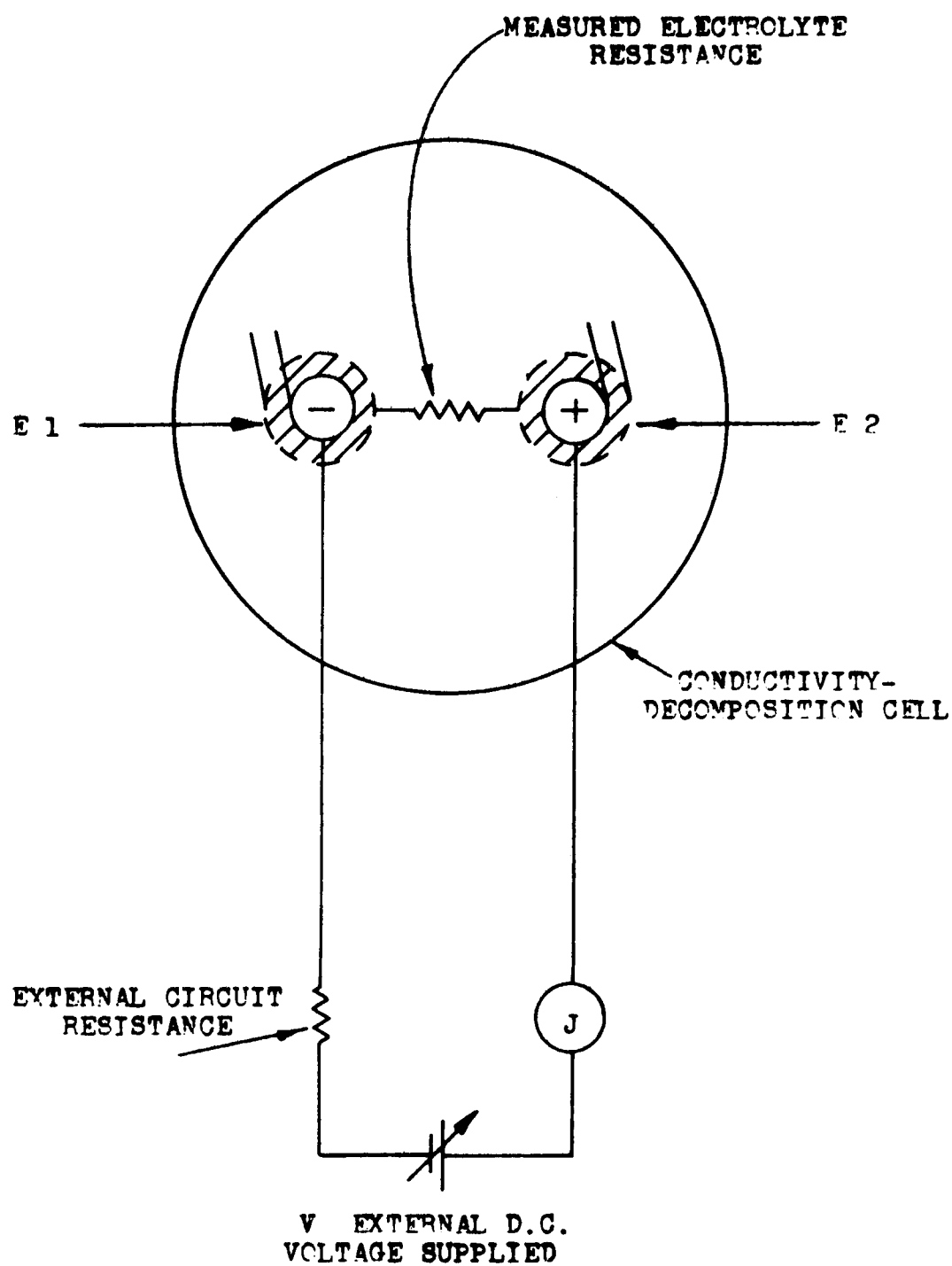
At the end of each voltage-current cycle, the cells are reset to initial conditions by short-circuiting the platinum electrodes for a period of three minutes. This cycle is repeated continuously until the reaction of the ligand is completed.

From the internal cell resistance and current data, the interfacial cell voltage X can be calculated according to the relationship:
$$X = V - I (R + R_m)$$
 where V is the applied voltage, I is the cell current, and R and R_m are the internal cell and series limiting resistances respectively.

At present, Tafel data are generated and recorded by the automatic equipment at a rate of about 5 current-voltage curves per hour per cell. This rate will be tripled by putting into operation equipment designed to vary environmental conditions and gather test data on nine conductivity cells simultaneously. Since this means that Tafel data will be generated at a rate in the order of 5,000 points per day, approaches for automatic data computation are being given urgent consideration.

*Complete recorder schematic Figure V, page 22.





ELECTRODE REACTION INTERFACE

PHYSICAL MODEL FOR SOLVENT ORIENTED BATTERY
ENERGY EQUATION

FIGURE III

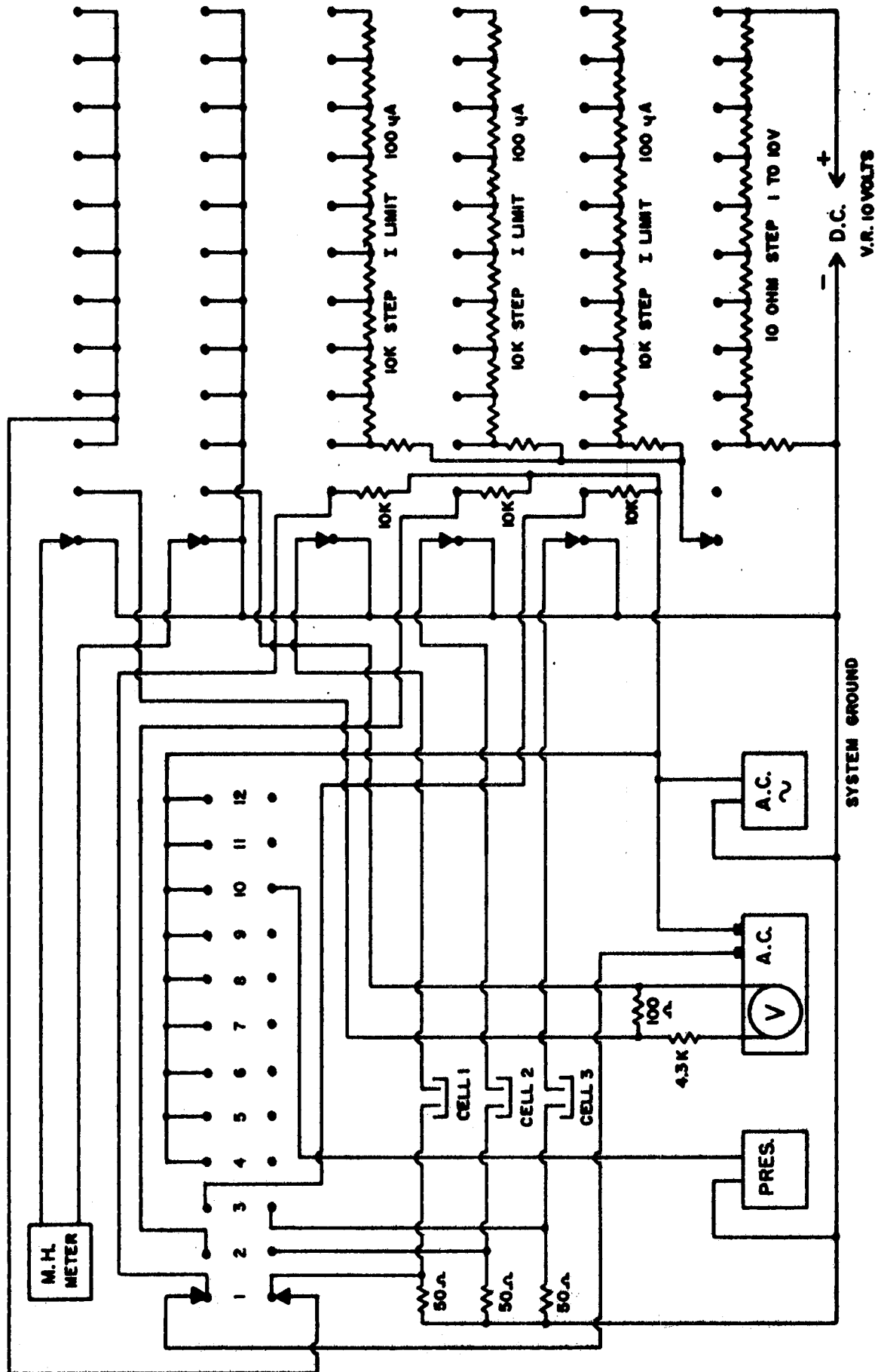


FIGURE V

Functional Schematic of Automatic Recording Equipment

(B) Evaluation of Solvent-Solute-Atmosphere Systems from Conductivity and Decomposition Potential Measurements

The figure of merit for a solvent-solute-atmosphere system as a battery electrolyte may be estimated from measured specific resistance, R , and modified Tafel constants C , and D in the equation:

$$X = C + D \ln J$$

where X is the sum of the two interfacial voltages E_1 and E_2 of Figure III on page 20, and J is the electrode current density I/A where I is the cell current and A is the geometric electrode area. Since D represents the slope of the Tafel line, a plot of X vs. $\log J$ is presently being made for each system under study; such a plot for the system is shown in Figure VI on page 24.

By utilizing the solvent oriented battery energy equation for the condition of 200 wh/lb. and an (arbitrary) inter-electrode spacing of 2 mm., the family of lines shown in Figure I on page 16 is obtained. For the system referred to in Figure VI where R was measured to be 2.1K and D was found to be .43, a minimum value of 7.3 is indicated for C in order for the system to be capable of the required performance.

The results obtained from the specific resistance and decomposition potential measurements demonstrate the ability of a coordinating atmosphere to significantly reduce the resistivity of several solvent-solute systems. For example, a sulphur dioxide atmosphere reduced the resistivity of lithium fluoride-isopropylamine solutions by a factor of 25.

ISOPROPYLAMINE + LiCl + SO₂ at 21.5 psia

Figure VI

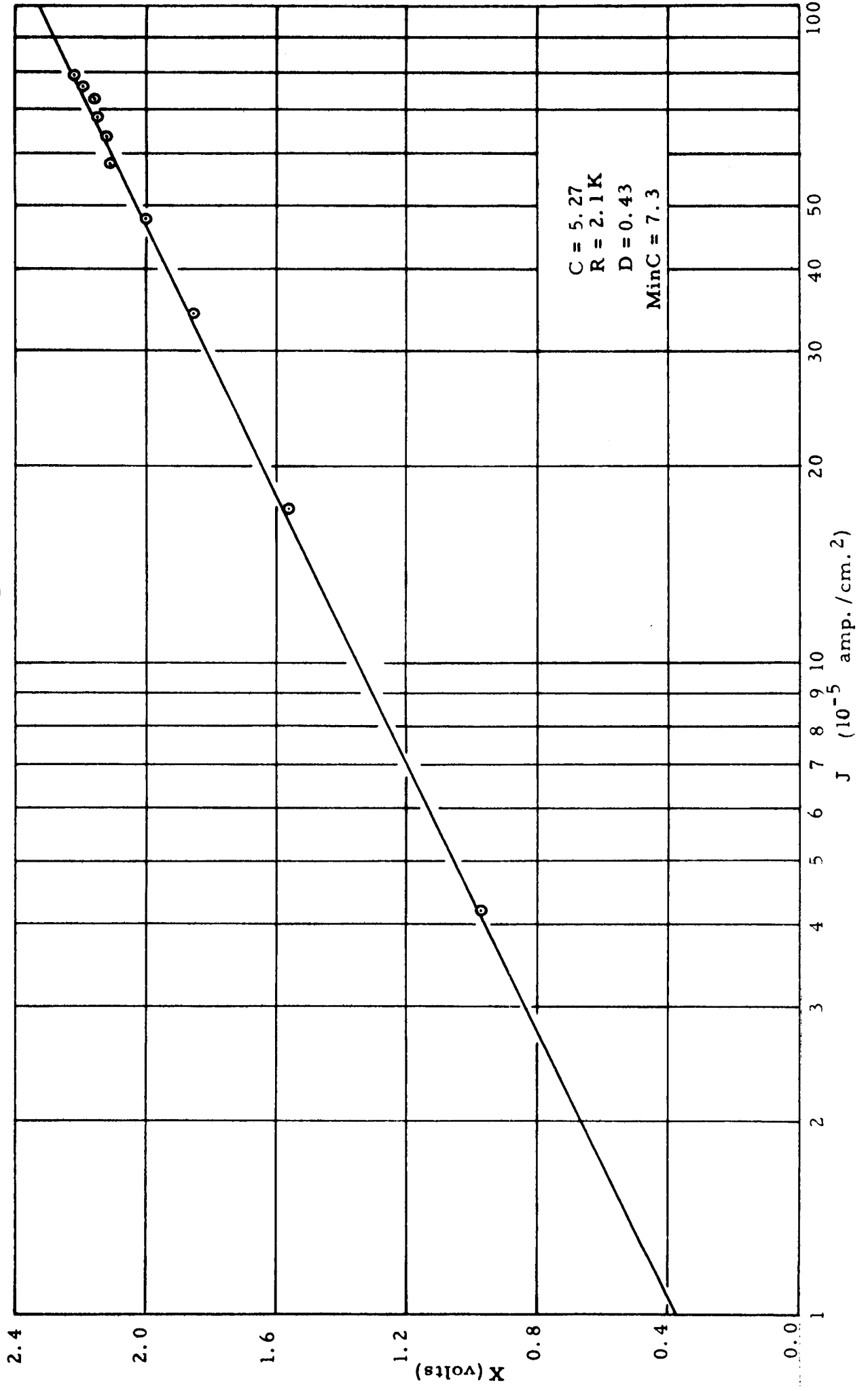


TABLE II

SPECIFIC RESISTANCE AND TAFEL DATA

P = Ligand partial pressure in pounds per square inch absolute

R = Electrolyte specific resistance kilohms

C = Electrolyte modified Tafel intercept (volts)

D = Electrolyte modified Tafel slope (volts)

n-Propylamine + NH₃(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	—	—	*
45	200	—	*
75	200	—	*
105	200	—	*
125	40	—	*

n-Propylamine + Lithium Chloride + NH₃(g)

0	7.0	—	**
45	3.0	4.0	0.4
75	3.0	3.0	0.3
105	3.0	3.3	0.3
135	1.0	4.1	0.4

n-Propylamine + Potassium Bromide + NH₃(g)

0	200	—	*
45	200	—	*
75	200	—	*
105	200	—	*
130	200	—	*

n-Propylamine + Tetramethyl Ammonium Chloride + NH₃(g)

0	200	—	*
45	200	—	*
75	200	—	*
105	200	—	*
130	200	—	*

*Tafel curve requires theoretical consideration; may be favorable.

**Tafel curve requires theoretical consideration; indications unfavorable.

TABLE II (continued)

<u>Butyrolactone + NH₃ (g)</u>	<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
	0	4.0	1.7	0.0
	45	7.0	2.9	0.2
<u>Butyrolactone + Lithium Chloride + NH₃(g)</u>				
	0	4.0	8.5	0.5
	45	2.0	3.8	0.3
	75	2.0	—	**
	105	2.0	3.8	0.3
<u>Butyrolactone + Aluminum Chloride + NH₃ (g)</u>				
	0	1.0	3.0	0.2
	45	0.3	—	**
	75	0.3	—	**
	105	0.3	2.7	0.1
<u>Butyrolactone + Magnesium Sulfate + NH₃(g)</u>				
	0	4.0	6.3	0.2
	45	2.0	5.5	0.7
	75	2.0	—	**
	105	2.0	4.0	0.4
<u>Butyrolactone + Potassium Bromide + NH₃(g)</u>				
	0	40	—	**
	45	40	—	**
	75	40	—	**
	105	10	—	**
	125	7.0	—	**
<u>Butyrolactone + Tetramethyl Ammonium Chloride + NH₃(g)</u>				
	0	200	—	**
	45	90	—	**
	75	90	2.7	0.2
	105	20	—	**
	125	20	—	**

TABLE II (continued)

Pyridine + NH₃(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	200	—	*
45	90	—	*
75	90	—	*
105	40	—	*
130	4.0	—	*

Pyridine + Lithium Chloride + NH₃(g)

0	7.0	4.0	0.5
45	7.0	2.1	0.2
75	7.0	2.4	0.2
105	7.0	1.8	0.1
135	4.0	2.8	0.2

Pyridine + Tetramethyl Ammonium Chloride + NH₃(g)

0	200	—	**
45	200	—	**
75	90	—	**
105	20	—	**
130	3.0	—	**

Pyridine + Potassium Bromide + NH₃(g)

0	90	—	*
45	200	—	*
75	200	—	*
105	100	—	*
135	40	—	*

N-Methyl-2-Pyrrolidone + NH₃(g)

0	40	—	**
45	40	—	**
75	20	—	**
105	10	—	**
120	7.0	—	**

N-Methyl-2-Pyrrolidone + Lithium Chloride + NH₃(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	1000	4.7	0.4
45	1000	—	**
75	1000	—	**
105	1000	—	**

N-Methyl-2-Pyrrolidone + Aluminum Chloride + NH₃(g)

0	10	1.5	0.1
45	40	—	**
75	20	—	**
105	10	2.1	0.1
135	4.0	3.9	0.3

N-Methyl-2-Pyrrolidone + Magnesium Sulfate + NH₃(g)

0	500	—	*
45	500	—	*
75	40	—	*
105	40	—	*
135	20	—	*

N-Methyl-2-Pyrrolidone + Potassium Bromide + NH₃(g)

0	10	4.0	0.3
---	----	-----	-----

N-Methyl-2-Pyrrolidone + Tetramethyl Ammonium Chloride + NH₃(g)

0	40	—	**
---	----	---	----

Propylene Carbonate + NH₃(g)

0	7.0	—	**
45	7.0	—	**
75	10	—	**
105	7.0	—	**

Propylene Carbonate + Lithium Chloride + NH₃(g)

0	20	—	**
45	20	—	**
75	20	—	**
105	20	—	**

TABLE II (continued)

Propylene Carbonate + Aluminum Chloride + NH₃(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	0.7	5.1	0.4
45	0.7	4.4	0.3
75	0.7	2.7	0.2
105	0.7	2.2	0.1

Propylene Carbonate + Magnesium Sulfate + NH₃(g)

0	100	—	**
45	30	—	**
75	20	—	**
105	30	—	**

Toluene + NH₃(g)

0	2000	—	*
45	2000	—	*
75	2000	—	*
105	2000	—	*

Toluene + Lithium Chloride + NH₃(g)

0	1000	—	*
45	1000	—	*
75	1000	—	*
105	2000	—	*

Toluene + Aluminum Chloride + NH₃(g)

0	1000	—	*
45	1000	—	*
75	1000	—	*
105	2000	—	*

Toluene + Potassium Bromide + NH₃(g)

0	1000	—	*
45	2000	—	*
75	2000	—	*
105	2000	—	*

<u>Toluene + Tetramethyl Ammonium Chloride + NH₃(g)</u>				
	<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
	0	2000	—	*
	45	2000	—	*
	75	2000	—	*
	105	2000	—	*
<u>Petroleum Ether + NH₃(g)</u>				
	0	2000	—	*
	45	2000	—	*
	75	2000	—	*
	105	2000	—	*
<u>Petroleum Ether + Lithium Chloride + NH₃(g)</u>				
	0	2000	—	*
	45	2000	—	*
	75	2000	—	*
	105	2000	—	*
<u>Methanol + NH₃(g)</u>				
	0	7.0	3.8	0.3
<u>Methanol + Lithium Chloride + NH₃(g)</u>				
	0	0.2	3.0	0.2
<u>Methanol + Potassium Bromide + NH₃(g)</u>				
	0	0.2	3.1	0.2
<u>Cyclohexanone + Lithium Chloride + NH₃(g)</u>				
	0	6.0	4.7	0.5
	45	9.0	5.0	0.4
	75	9.0	3.7	0.6
<u>Hexylene Glycol + NH₃(g)</u>				
	0	1000	—	*
<u>Hexylene Glycol + Lithium Chloride + NH₃(g)</u>				
	0	30	4.3	0.2

Petroleum Ether + Potassium Iodide + SO₂(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	—	—	**
39.0	—	—	*
41.2	—	—	*
46.0	50	—	*
47.5	48	—	*
48.0	48	—	*

Petroleum Ether + Tetramethyl Ammonium Chloride + SO₂(g)

0	—	—	**
39.0	—	—	*
41.2	45	—	*
46.0	46	—	*
47.5	46	—	*
48.0	46	—	*

Acetone + Lithium Chloride + SO₂(g)

0	2.0	0.2	3.1
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Cyclohexanone + Aluminum Chloride + NH₃(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	200	1.4	0.0
45	200	—	**
75	200	—	**
105	200	—	**

Isopropylamine + Aluminum Chloride + SO₂(g)

0	7.8	4.7	0.4
16.0	8.2	6.9	0.6
20.0-19.0	10	6.7	0.6
20.5-22.4	16	16	1.9
26.5-28.5	21	37	4.3
31.0-32.0	21	74	8.8
33.0	19	130	12
35.0-36.4	12	88	9.1
39.0-39.4	10	130	12
42.0-42.9	5.9	97	10
49.0	2.9	119	12
45.0	1.6	66	7.0
43.0	1.1	27	2.7

Isopropylamine + Lithium Fluoride + SO₂(g)

0	45	22	2.4
16.0	125	13	1.4
20.0-19.0	150	48	4.5
20.5-22.4	125	—	**
26.5-28.5	13	—	**
31.0-32.0	9.8	—	**
33.0	11	—	**
35.0-36.4	11	—	**
39.0-39.4	9	137	15
42.0-42.9	6.9	71	6.8
49.0	2.8	198	21
45.0	2.5	76	7.5
43.0	2.8	105	10

Isopropylamine + Lithium Chloride + SO₂(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	1.8	4.7	0.4
16.0	1.8	7.3	0.7
20.0-19.0	2.0	5.1	0.4
20.5-22.4	2.1	5.3	0.4
26.5-28.5	2.8	6.8	0.7
31.0-32.0	2.8	5.8	0.6
33.0	2.8	9.6	1.0
35.0-36.4	2.8	13	1.4
39.0-39.4	2.4	138	14
42.0-42.9	2.8	90	8.6
49.0	2.8	145	14
45.0	3.0	101	9.1
43.0	3.3	55	5.4

Propylene Carbonate + SO₂(g)

0	8.5	6.1	0.7
—	140	—	**
—	50	—	**
—	49	—	**

Propylene Carbonate + Potassium Iodide + SO₂(g)

0	1.5	66	8.2
—	48	31	3.1
—	55	20	1.9
—	50	28	2.3

Propylene Carbonate + Tetramethyl Ammonium Chloride + SO₂(g)

0	1.8	7.6	0.6
—	50	—	**
—	50	—	**
—	49	—	**

Propylene Carbonate + Lithium Fluoride + SO₂(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	3.9	11	1.6
20.5	0.7	33	2.9
21.5	0.7	30	3.8
22.0	0.8	8.9	0.9
22.5	1.0	14	1.6
25.2	3.6	11	0.9
25.2	1.1	18	2.0
27.0	1.1	15	1.7
51.0	1.1	16	1.8
51.3	1.0	16	1.8
51.3	1.0	15	1.7
52.0	1.0	32	3.5
52.5	1.4	25	2.9

Propylene Carbonate + Lithium Chloride + SO₂(g)

0	17	7.3	1.1
20.5	15	17	2.1
21.5	15	16	3.3
22.0	15	17	2.1
22.5	12	14	1.8
25.2	11	18	2.2
25.2	11	18	2.2
27.0	11	26	3.3
51.0	11	16	1.9
51.3	11	18	2.3
51.3	11	31	4.0
52.0	11	30	2.4
52.5	11	15	1.8

Propylene Carbonate + Aluminum Chloride + SO₂(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	2.9	14	2.5
20.5	2.9	55	5.3
21.5	2.9	96	13.1
22.0	3.0	50	6.4
22.5	3.4	14	1.5
25.2	3.4	9.3	0.9
25.2	3.6	11	0.9
27.0	3.8	12	1.1
51.0	3.9	7.3	0.6
51.3	4.1	13	1.4
51.3	4.1	12	1.2
52.0	4.5	13	1.5
52.5	4.8	13	1.3

Propylene Carbonate + Potassium Bromide + SO₂(g)

0	75	32	3.7
37.5-39.0	4.8	3.8	0.3
42.5-43.0	6.8	—	**
43.0	7.2	2.7	0.2
43.0	7.8	2.7	0.2
46.0-48.0	7.9	6.2	0.7
49.0-50.0	8.6	3.0	0.2
51.0	100	—	**

Propylene Carbonate + Sodium Iodide + SO₂(g)

0	0.3	—	**
37.5-39.0	1.5	4.5	0.0
42.5-43.0	3.1	18	1.3
43.0	1.3	22	2.3
43.0	1.3	19	2.1
46.0-48.0	1.1	14	1.4
49.0-50.0	1.2	10	0.9
51.0	43	—	**

Propylene Carbonate + Tetramethyl Ammonium Chloride + SO₂(g)

<u>P</u>	<u>R</u>	<u>C</u>	<u>D</u>
0	0.1	54	5.2
37.5-39.0	0.4	4.0	0.3
42.5-43.0	0.9	1.7	0.1
43.0	1.2	—	**
43.0	1.3	2.2	1.4
46.0-48.0	1.1	2.1	0.1
49.0-50.0	1.1	2.3	0.1
51.0	41	—	**

Petroleum Ether + SO₂(g)

0	—	—	**
21.5-48.0	—	—	*

Petroleum Ether + Lithium Chloride + SO₂(g)

0	—	—	*
23.0-51.0	—	—	*

Petroleum Ether + Lithium Fluoride + SO₂(g)

0	—	—	*
23.0-51.0	—	—	*

Petroleum Ether + Potassium Bromide + SO₂(g)

0	—	—	*
23.0-51.0	—	—	*

Petroleum Ether + Aluminum Chloride + SO₂(g)

0	—	—	**
39.0	—	—	*
41.2	—	—	*
46.0	—	—	*
47.5	—	—	*
48.0	—	—	*

GASEOUS ENERGY EQUATION

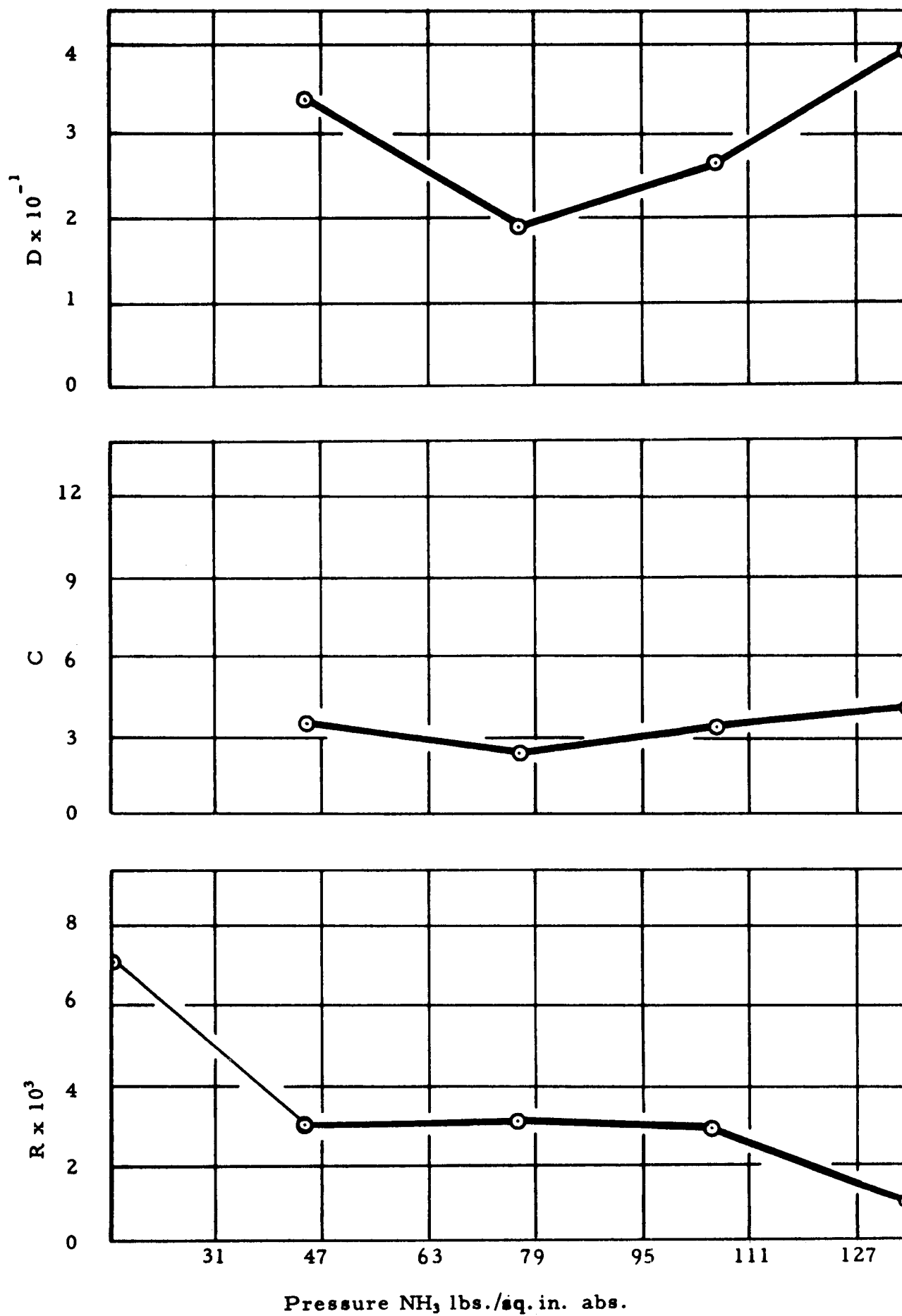
SPECIFIC RESISTANCE AND TAFEL DATA GRAPHS
BASED ON TABLE II

NOTE

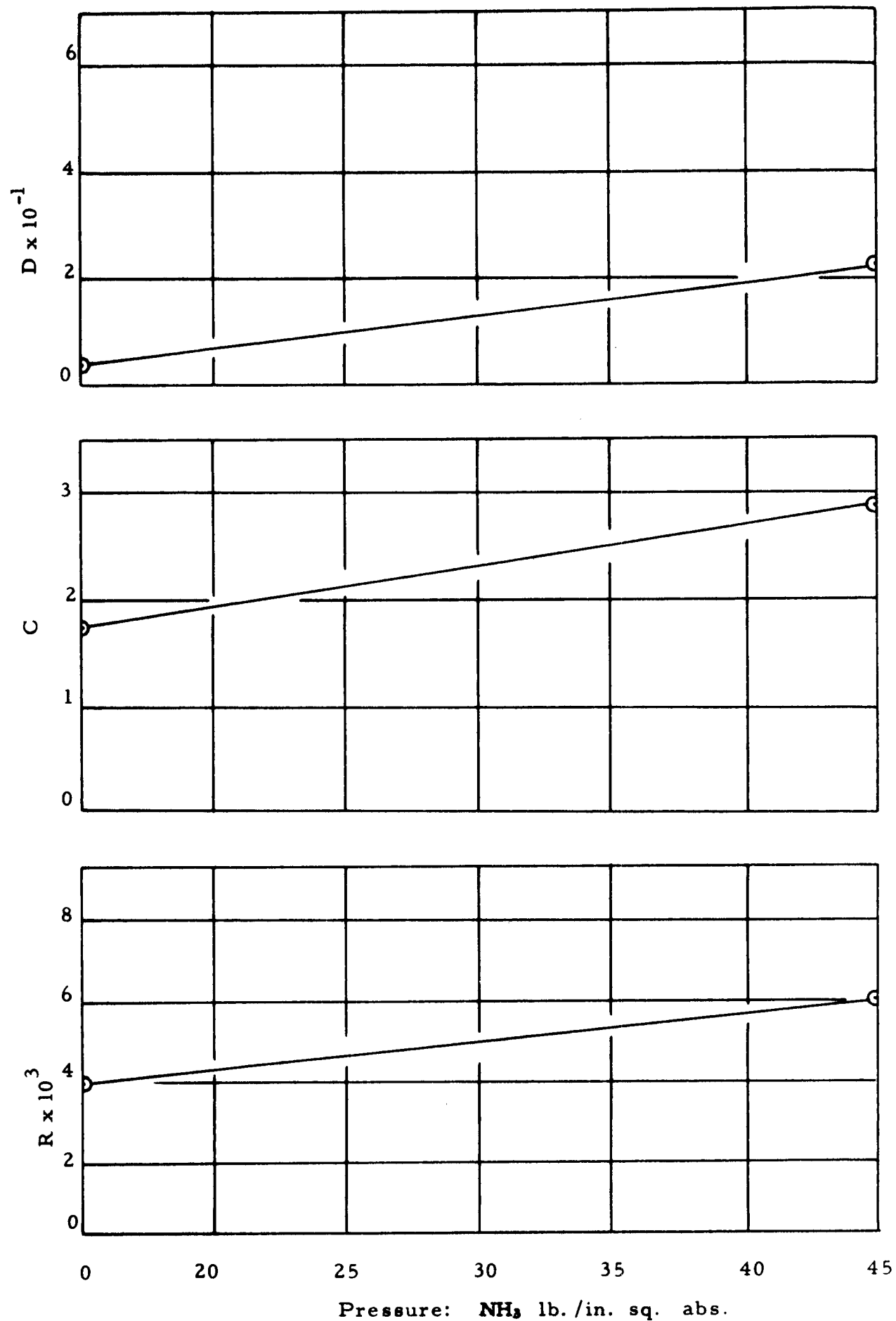
The R, C, and D values are plotted against ligand partial pressure on the following graphs.

The conductivity cell has an air atmosphere at "0" ligand partial pressure. The thin solid line indicates that "0" pounds per square inch absolute is only a point of reference. Dotted lines designate regions where C and D could not be determined.

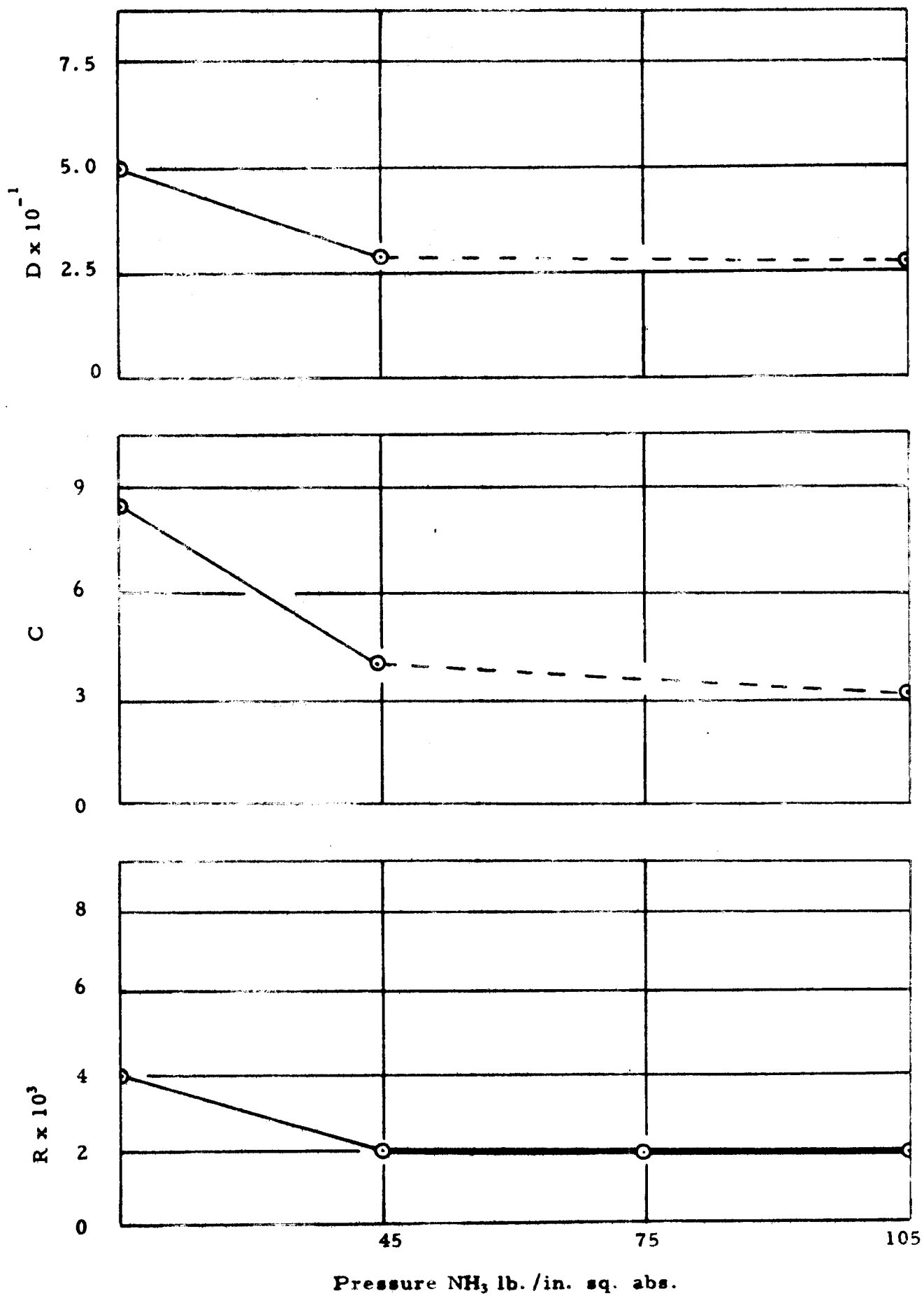
n-PROPYLAMINE + LITHIUM CHLORIDE



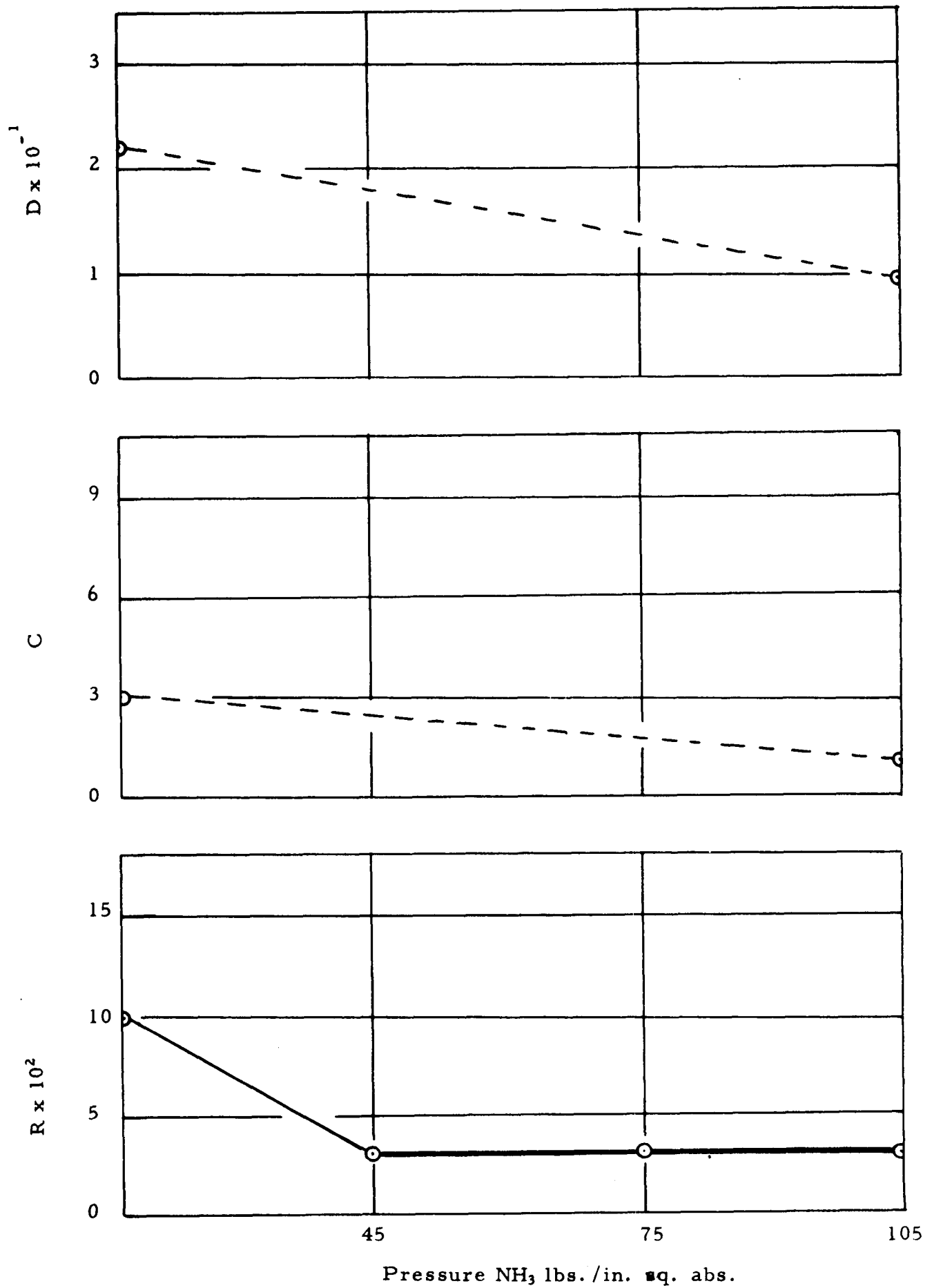
BUTYROLACTONE



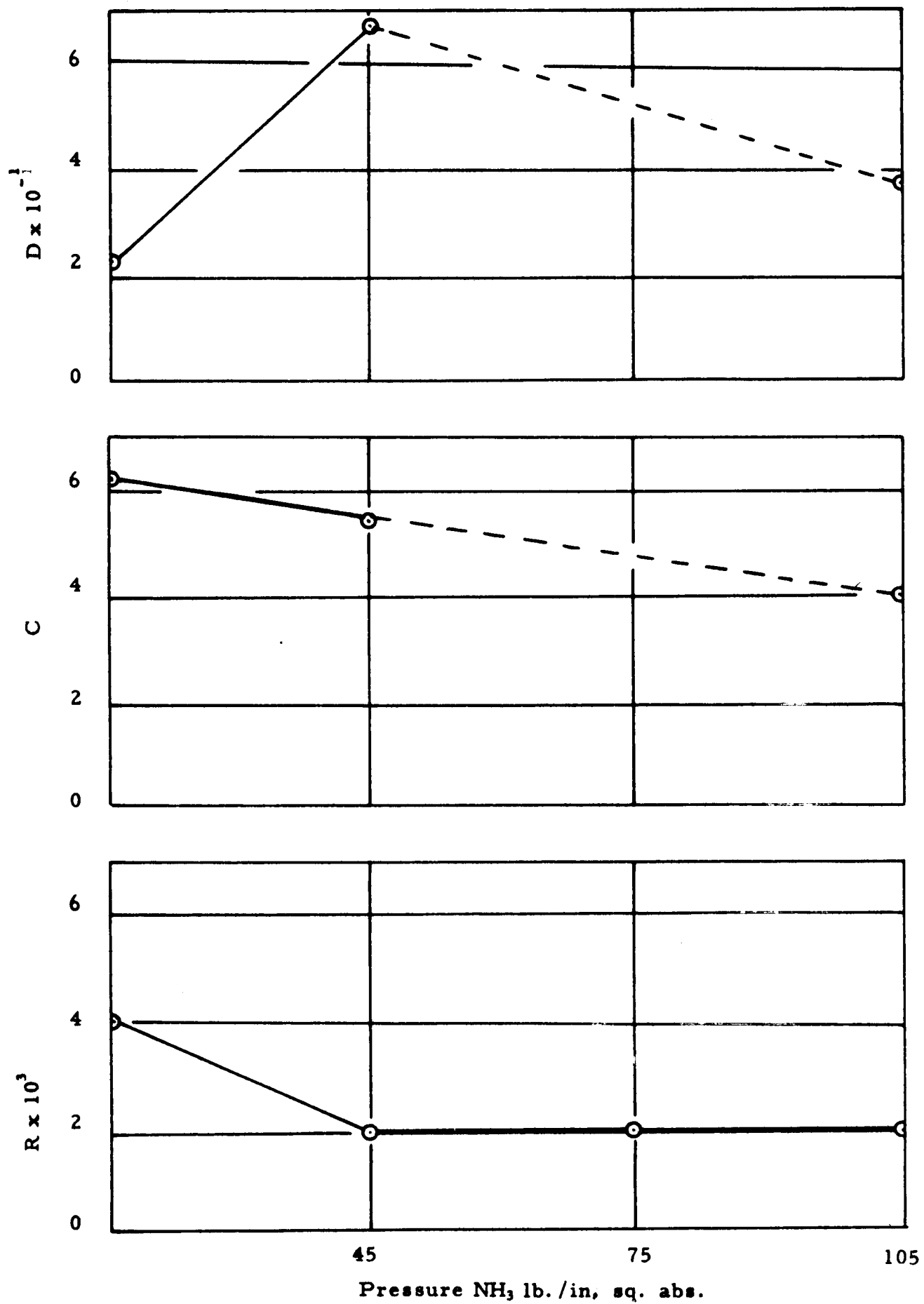
BUTYROLACTONE + LITHIUM CHLORIDE



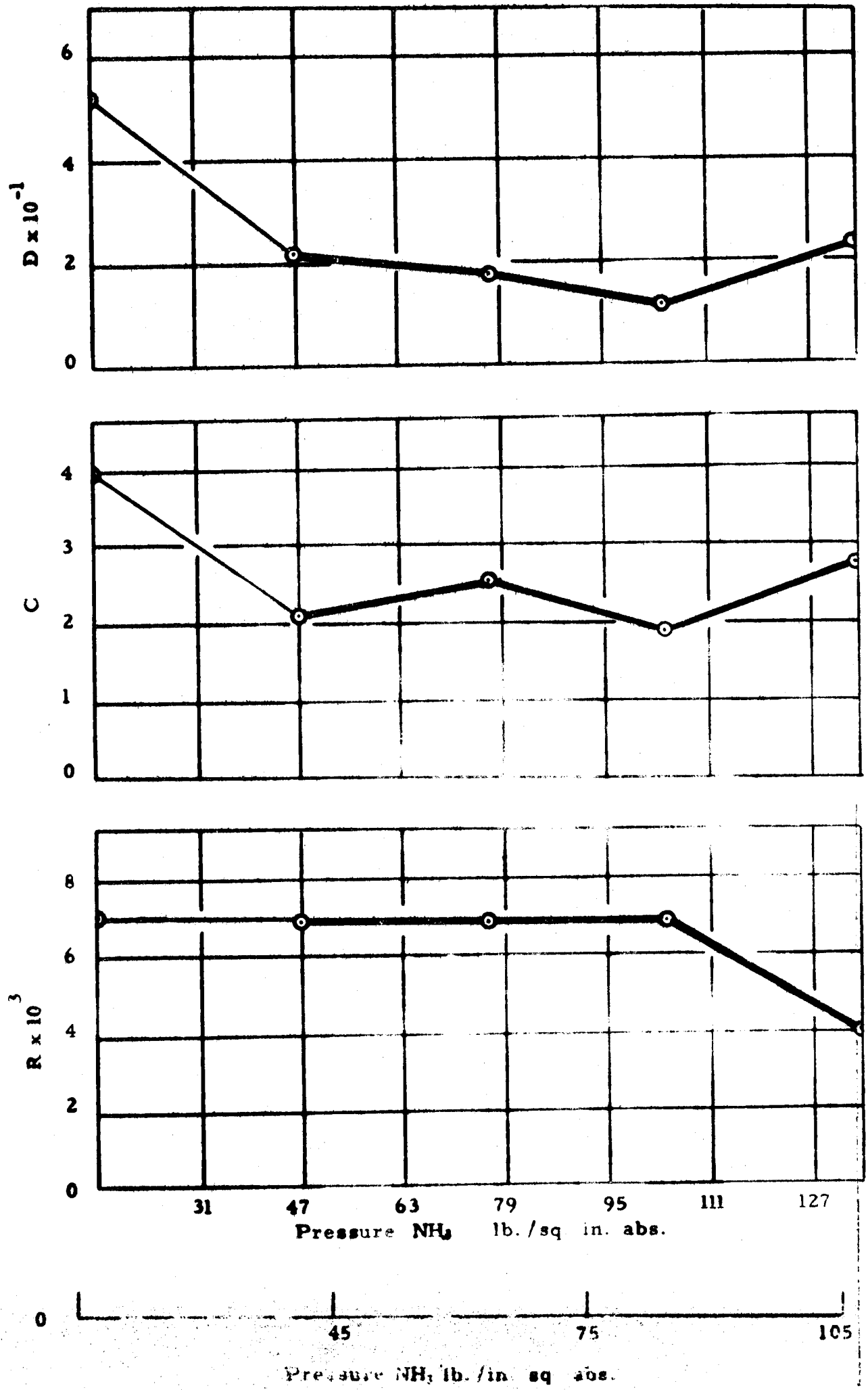
BUTYROLACTONE + ALUMINUM CHLORIDE



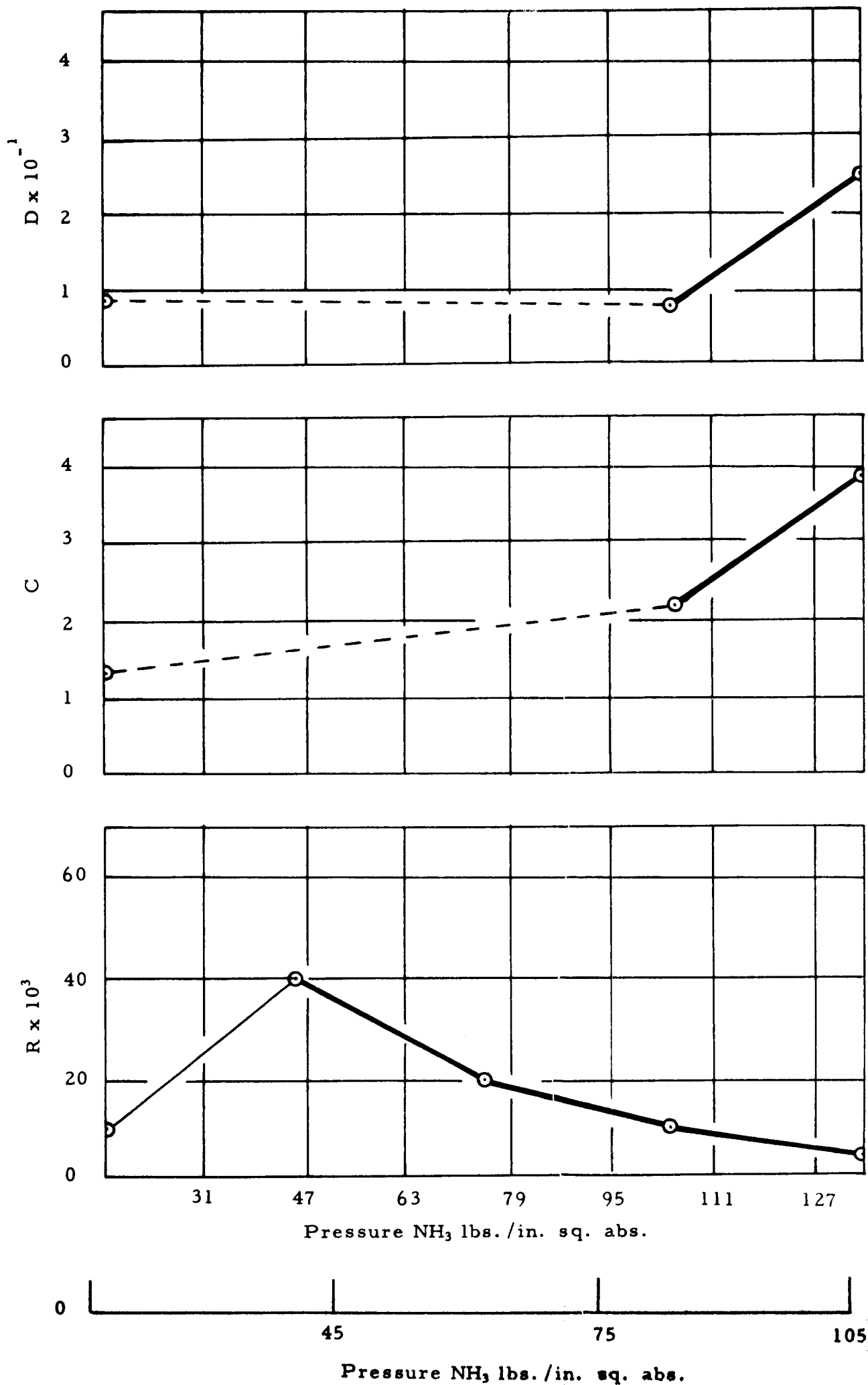
BUTYROLACTONE + MAGNESIUM SULFATE



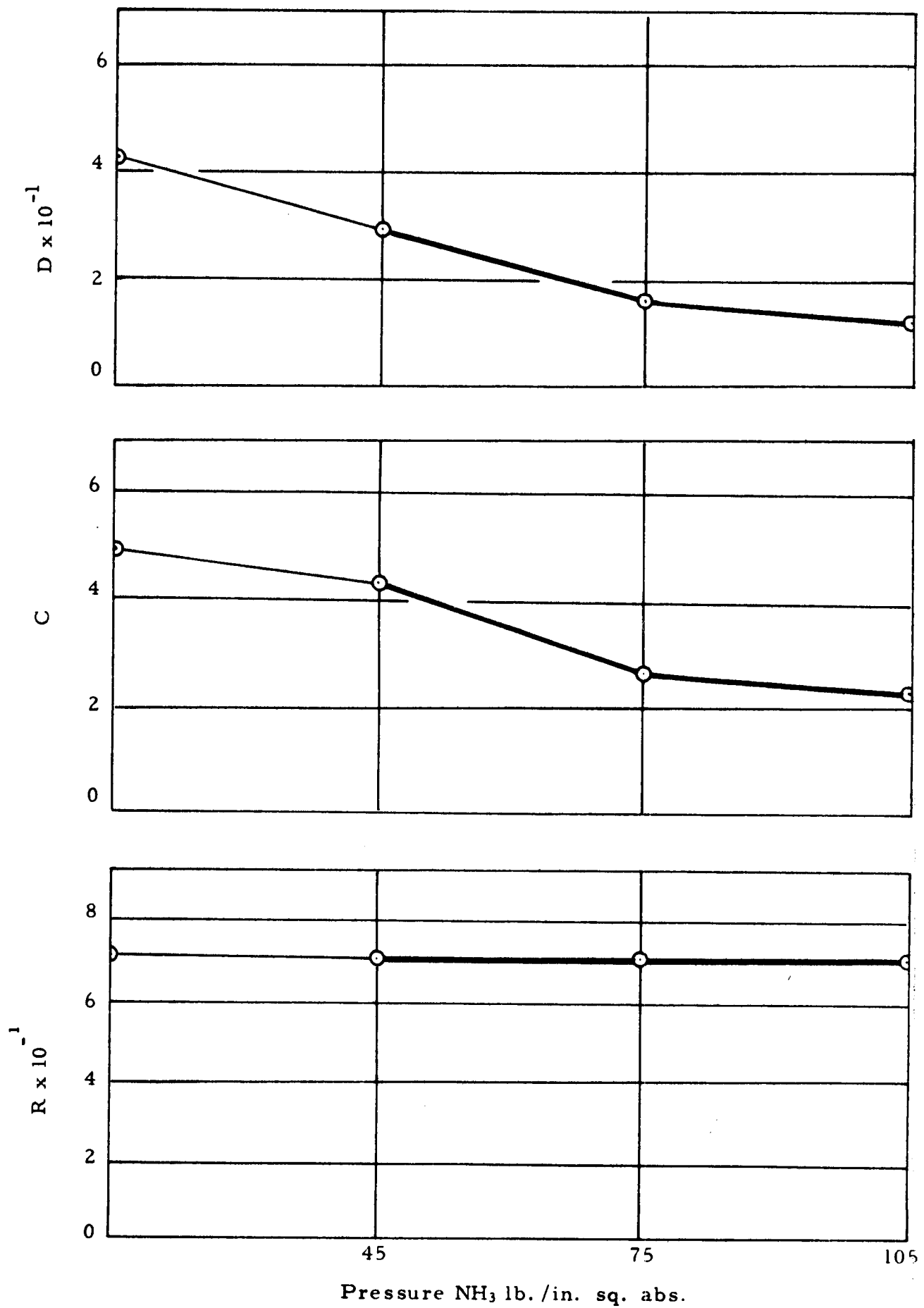
PYRIDINE + LITHIUM CHLORIDE



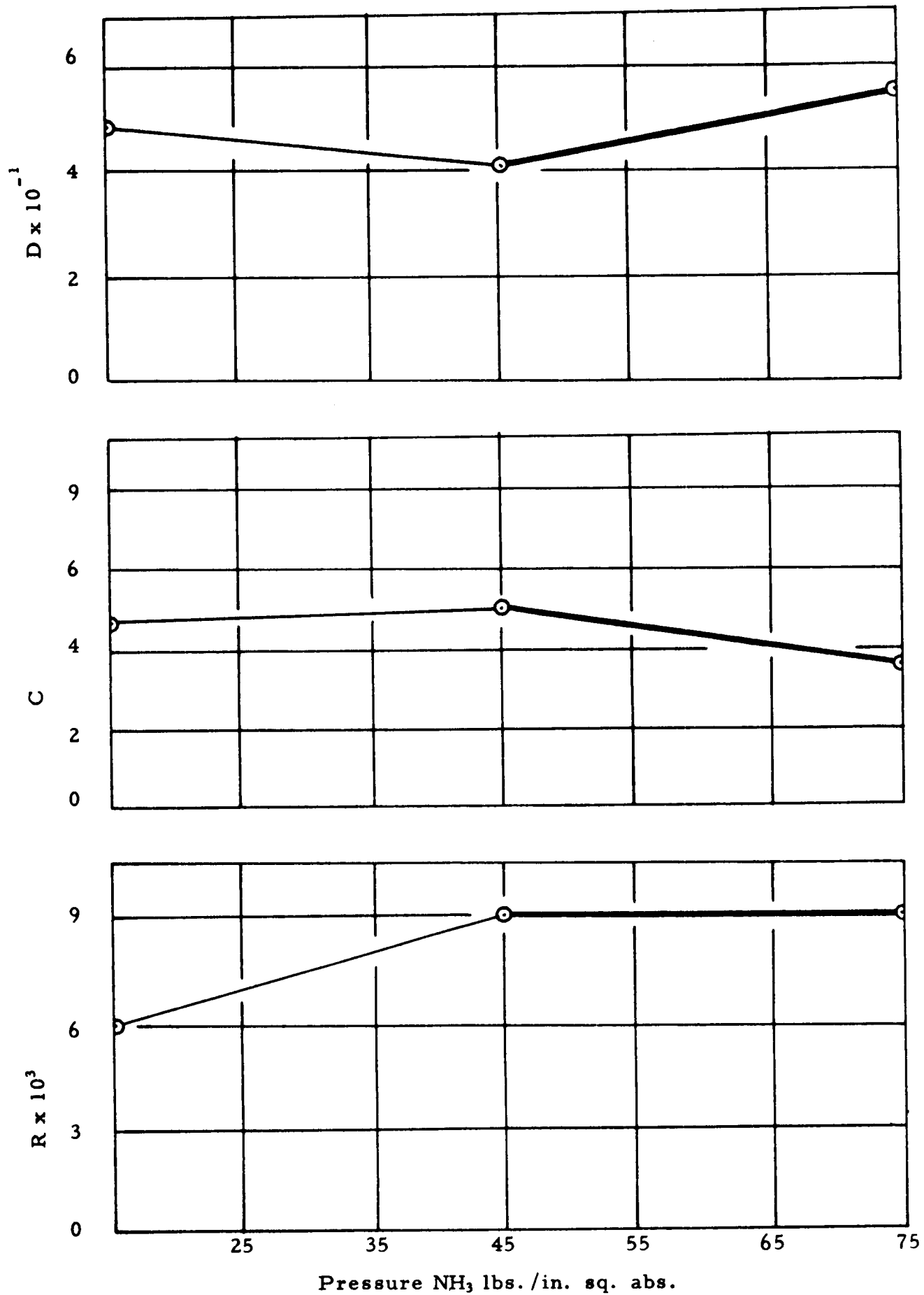
N-METHYL-2-PYRROLIDONE + ALUMINUM CHLORIDE



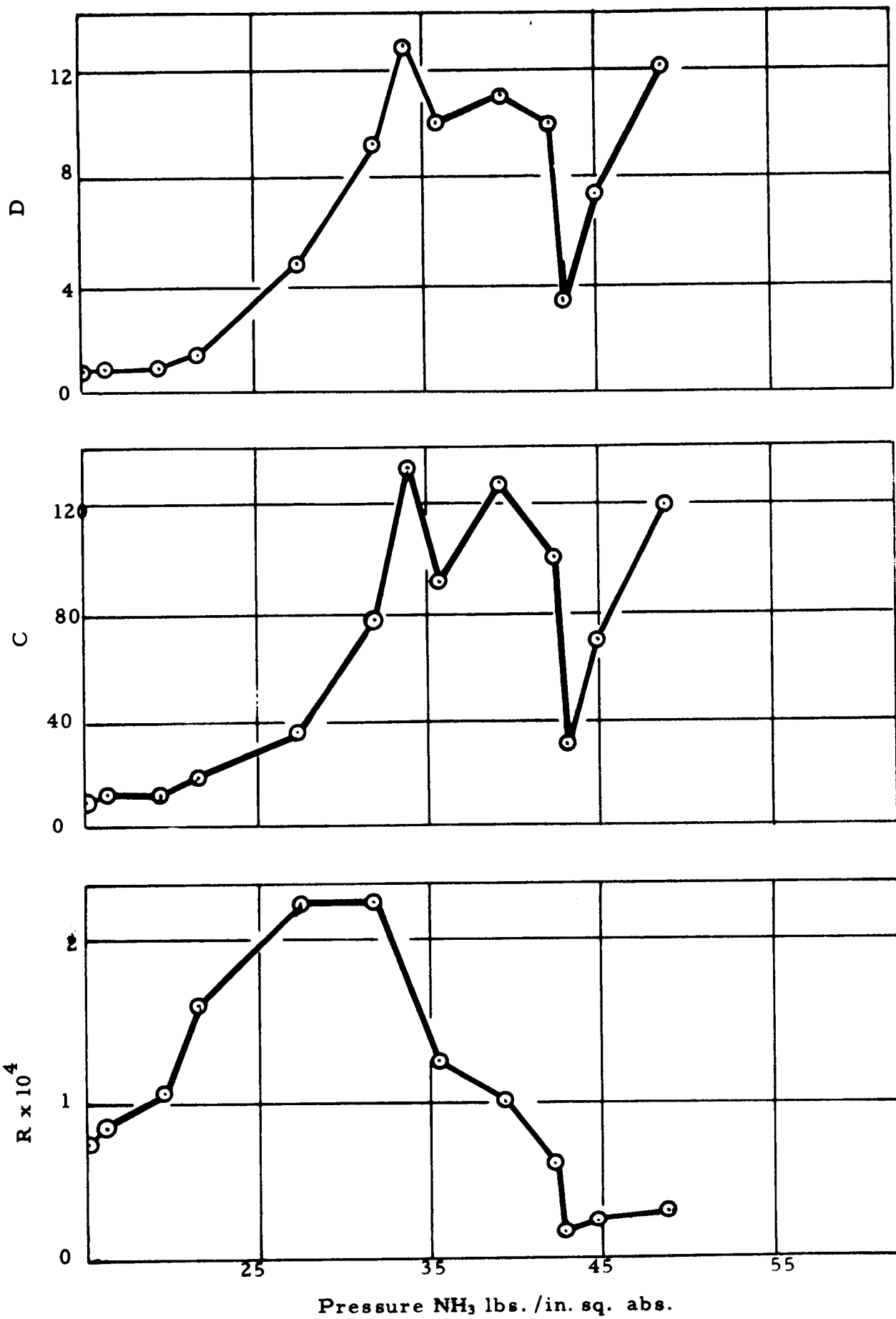
PROPYLENE CARBONATE + ALUMINUM CHLORIDE



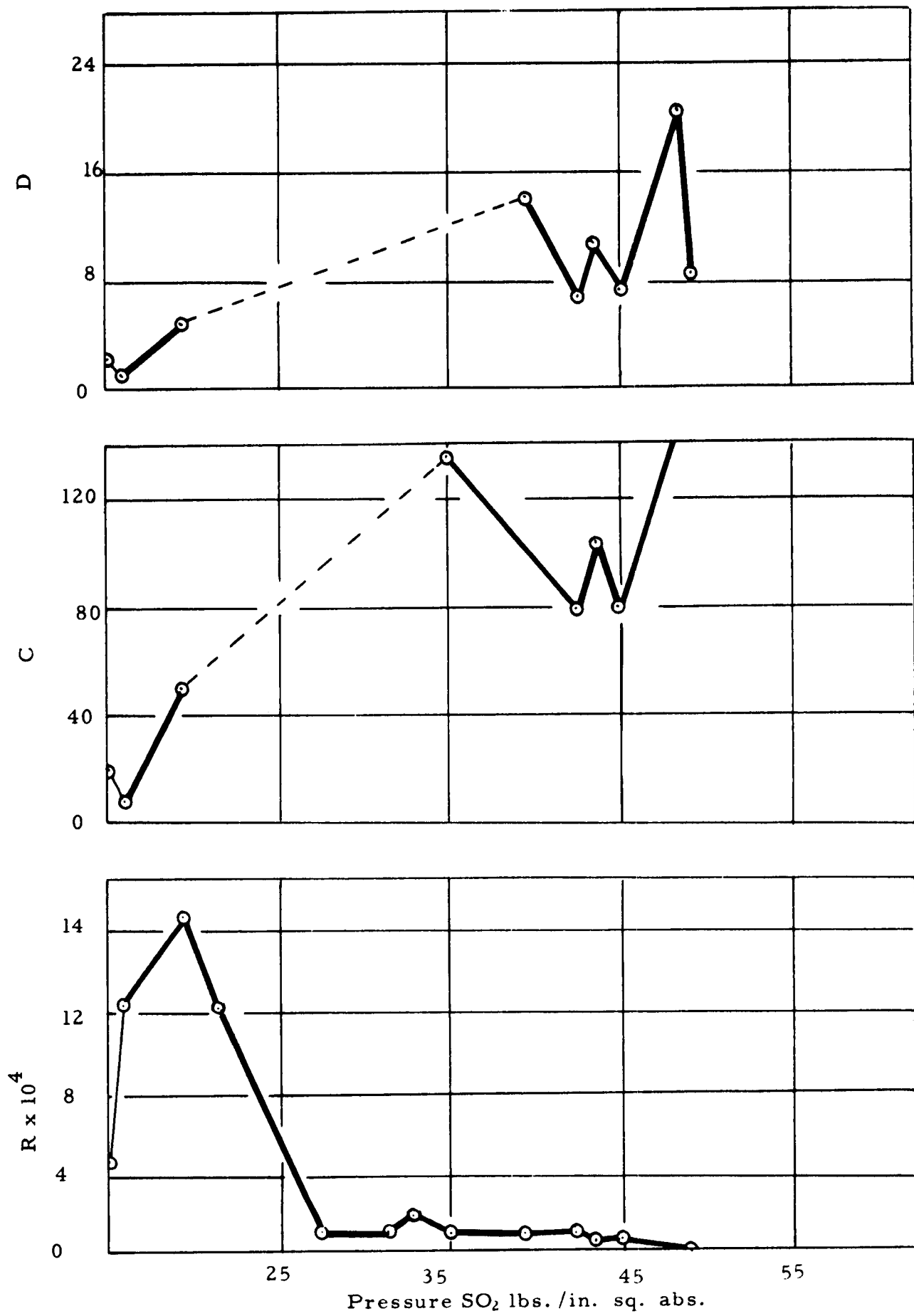
CYCLOHEXANONE + LITHIUM CHLORIDE



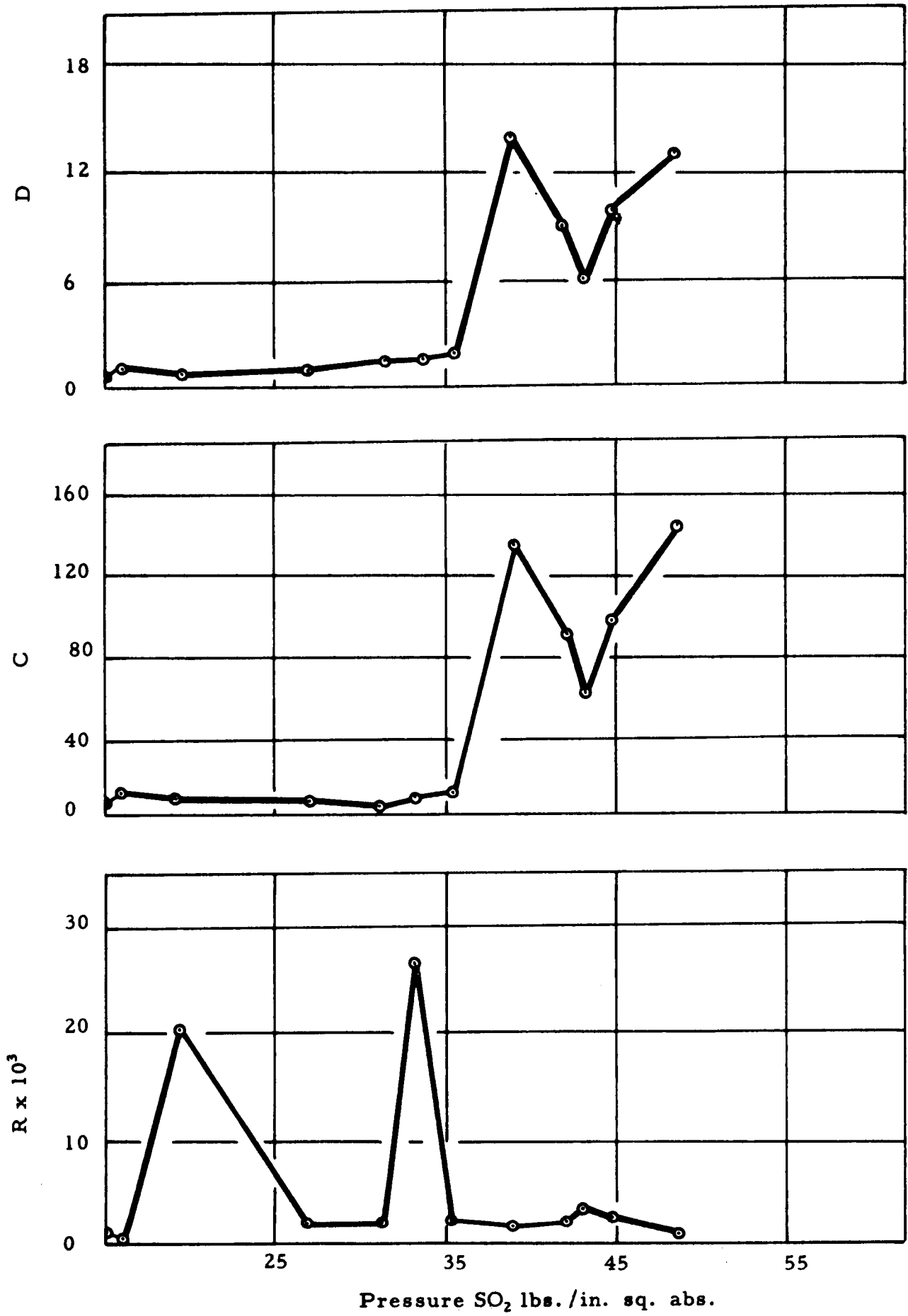
ISOPROPYLAMINE + ALUMINUM CHLORIDE



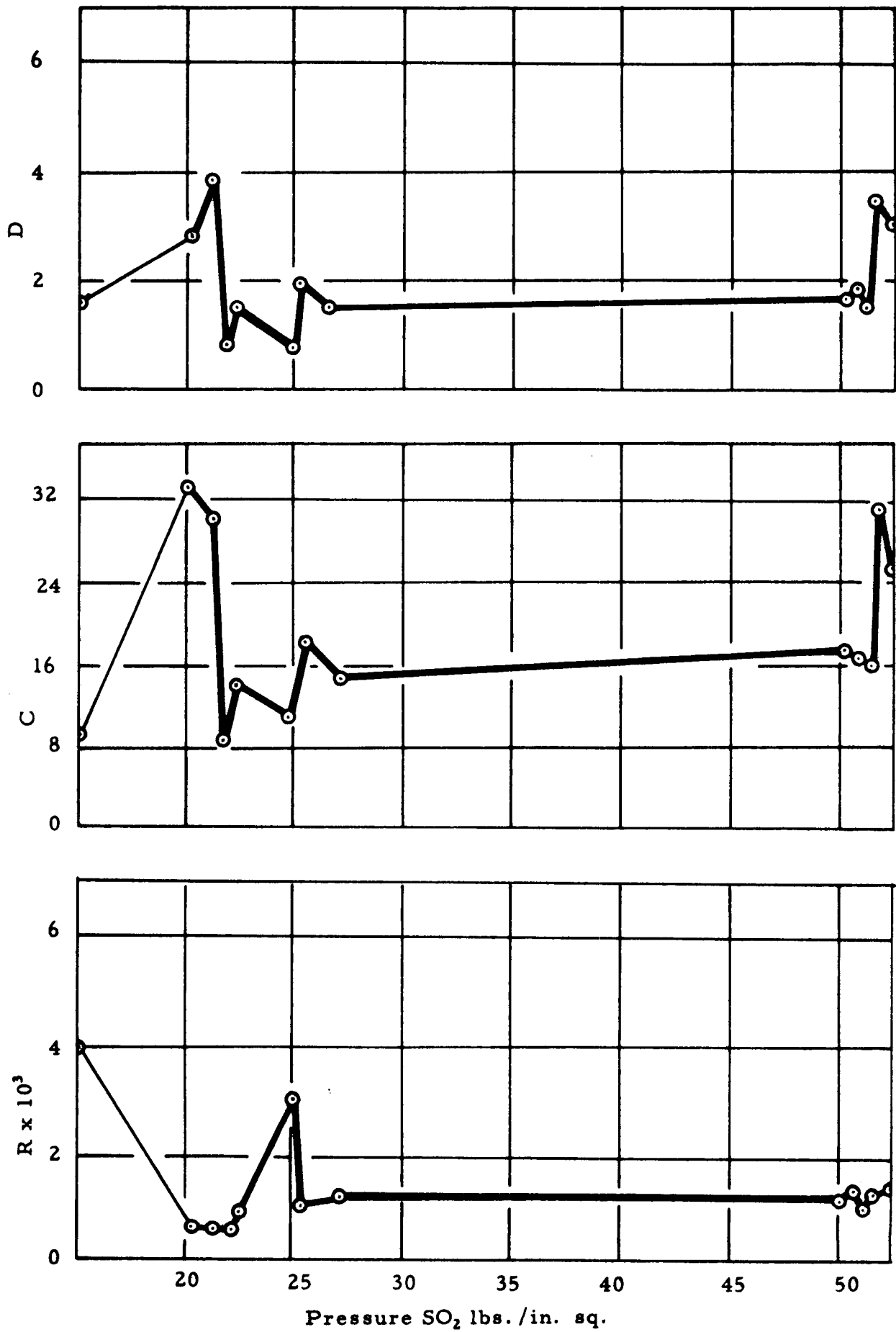
ISOPROPYLAMINE + LITHIUM FLUORIDE



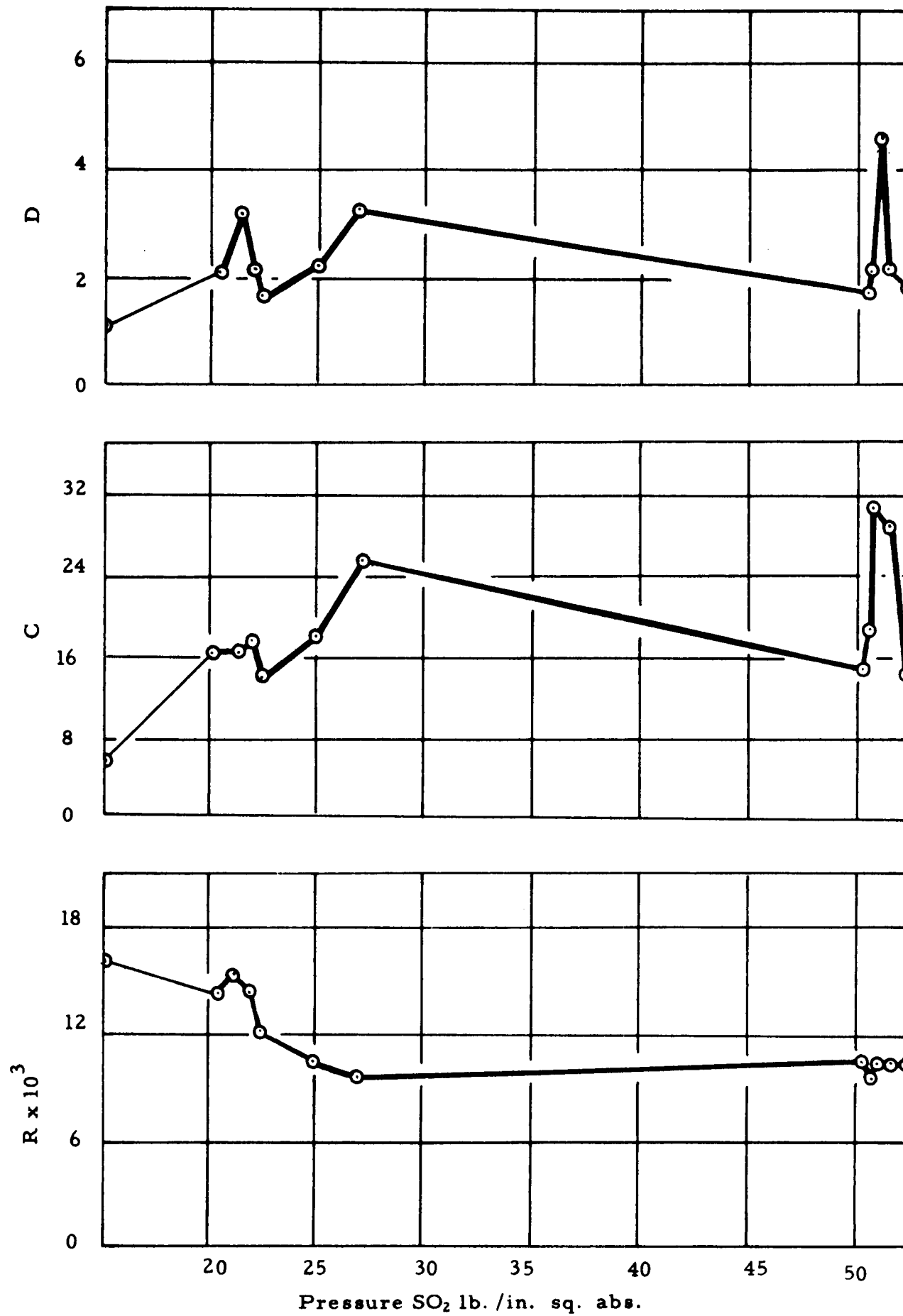
ISOPROPYLAMINE + LITHIUM CHLORIDE



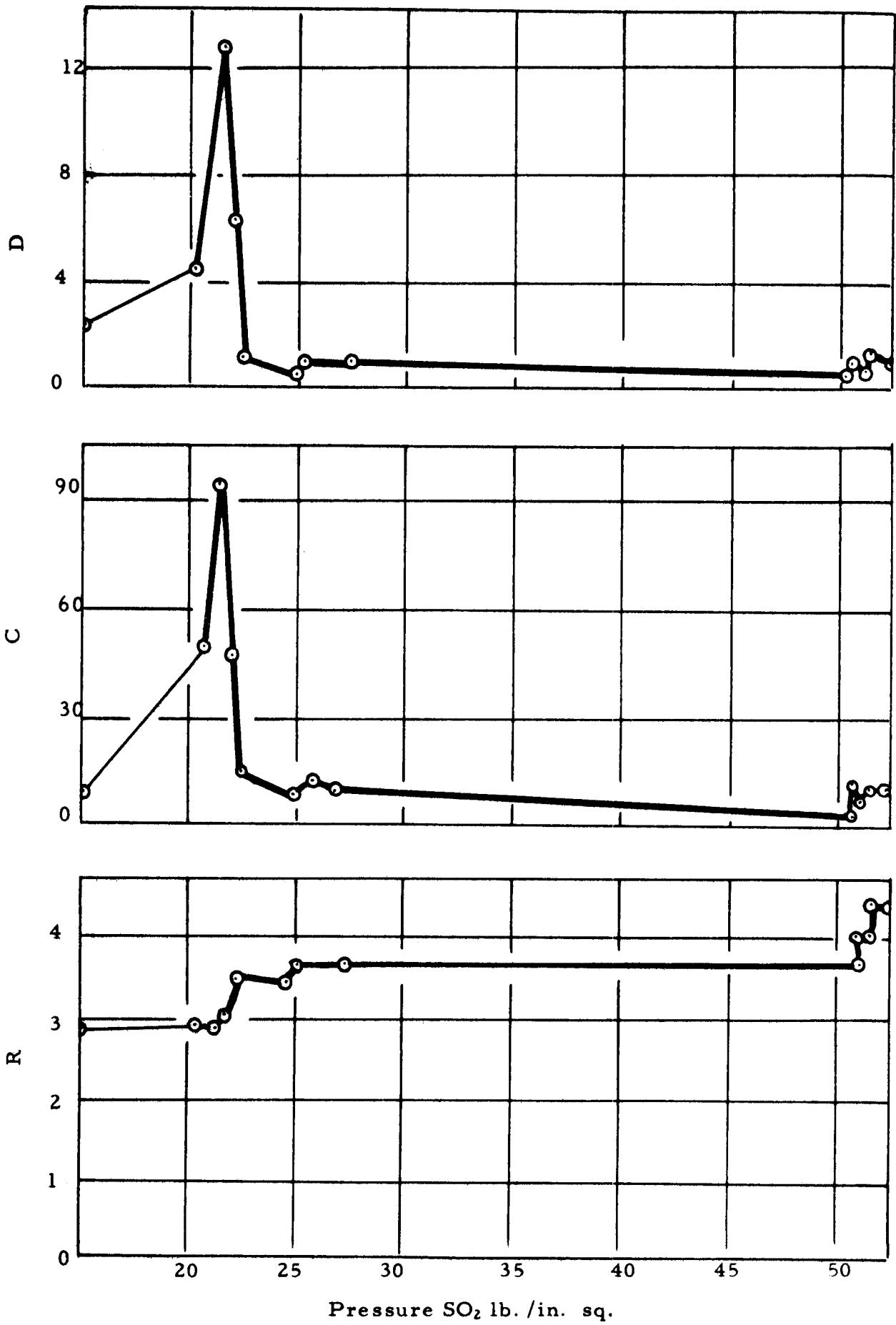
PROPYLENE CARBONATE + LITHIUM FLUORIDE



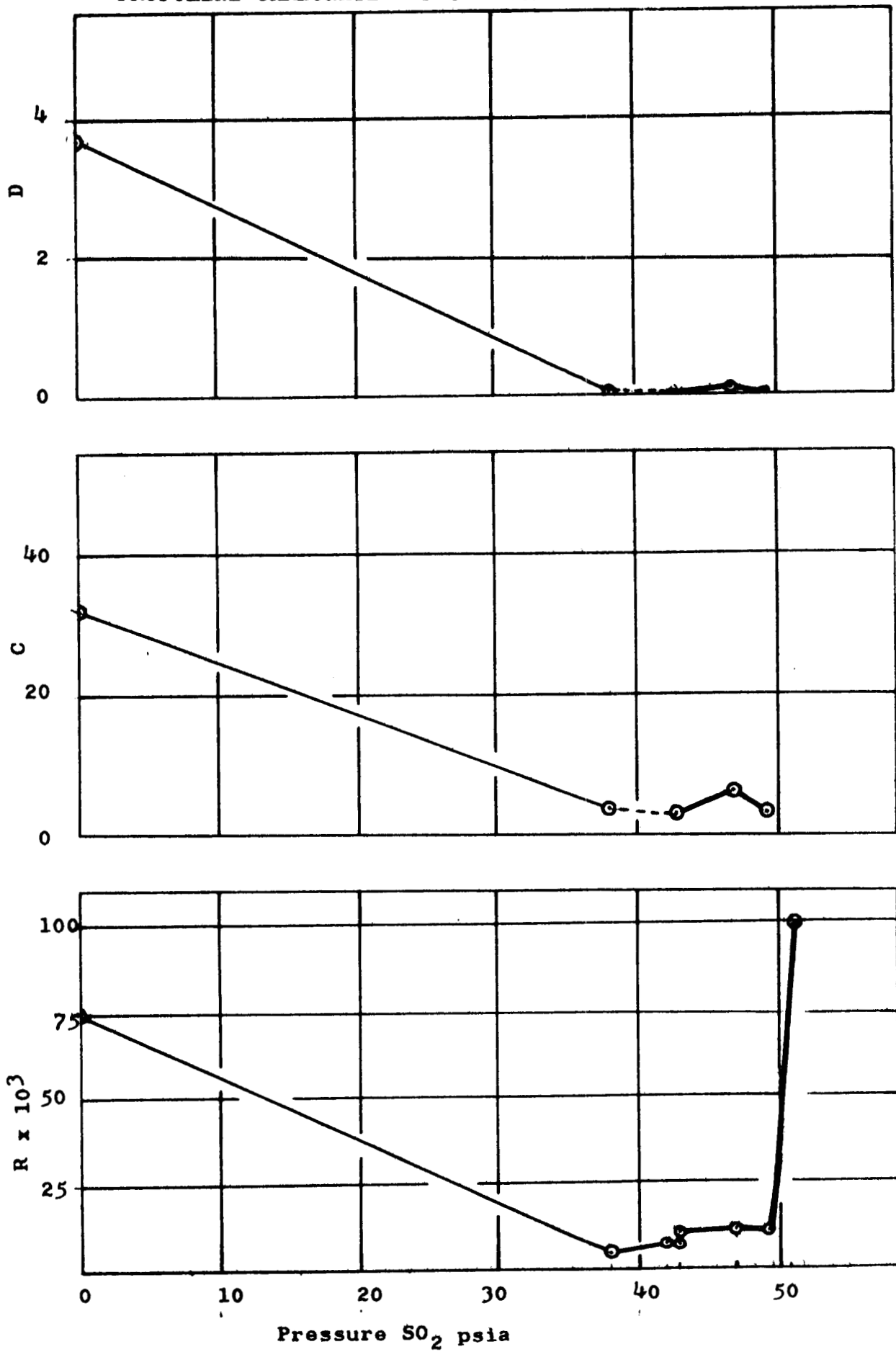
PROPYLENE CARBONATE + LITHIUM CHLORIDE



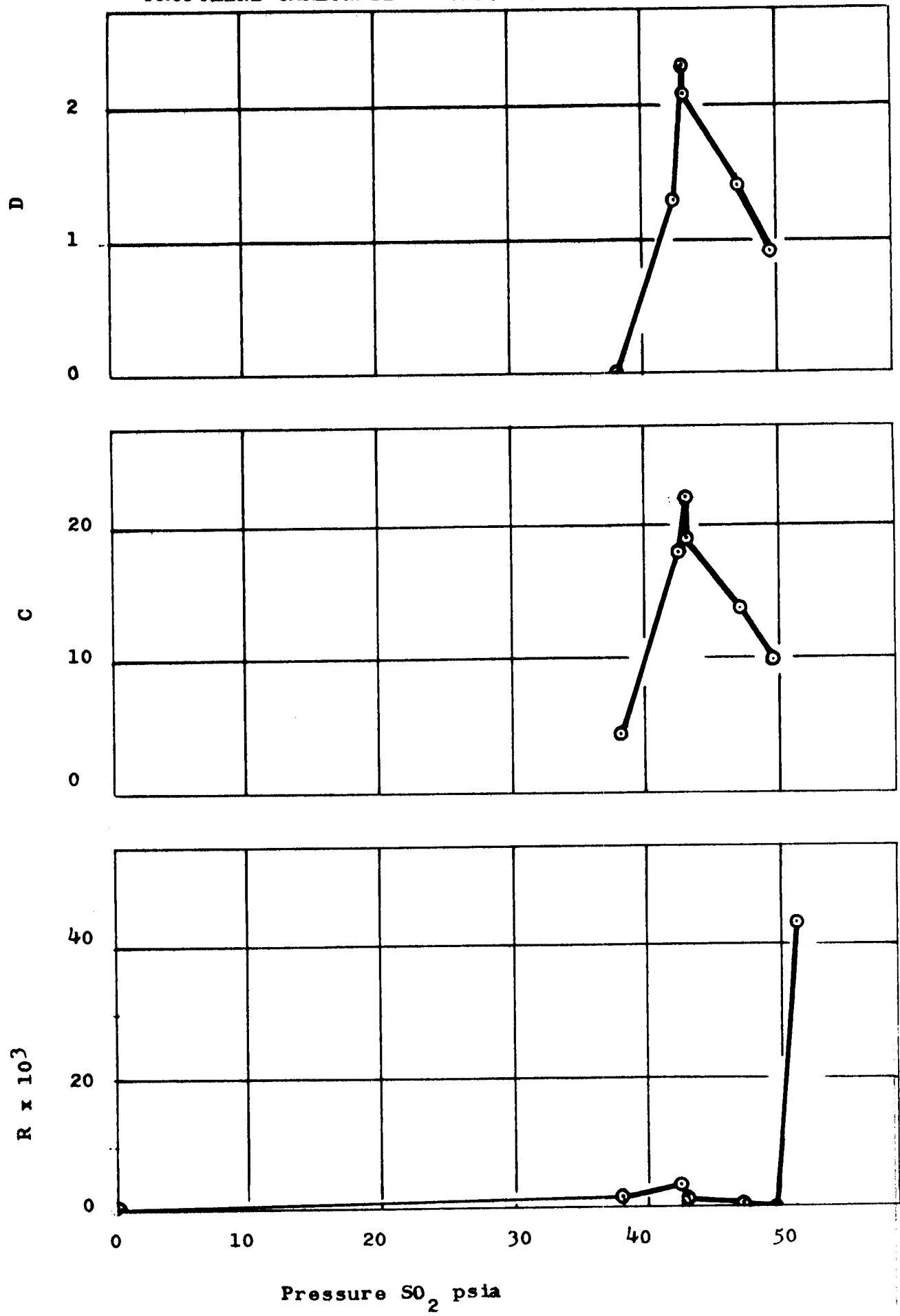
PROPYLENE CARBONATE + ALUMINUM CHLORIDE



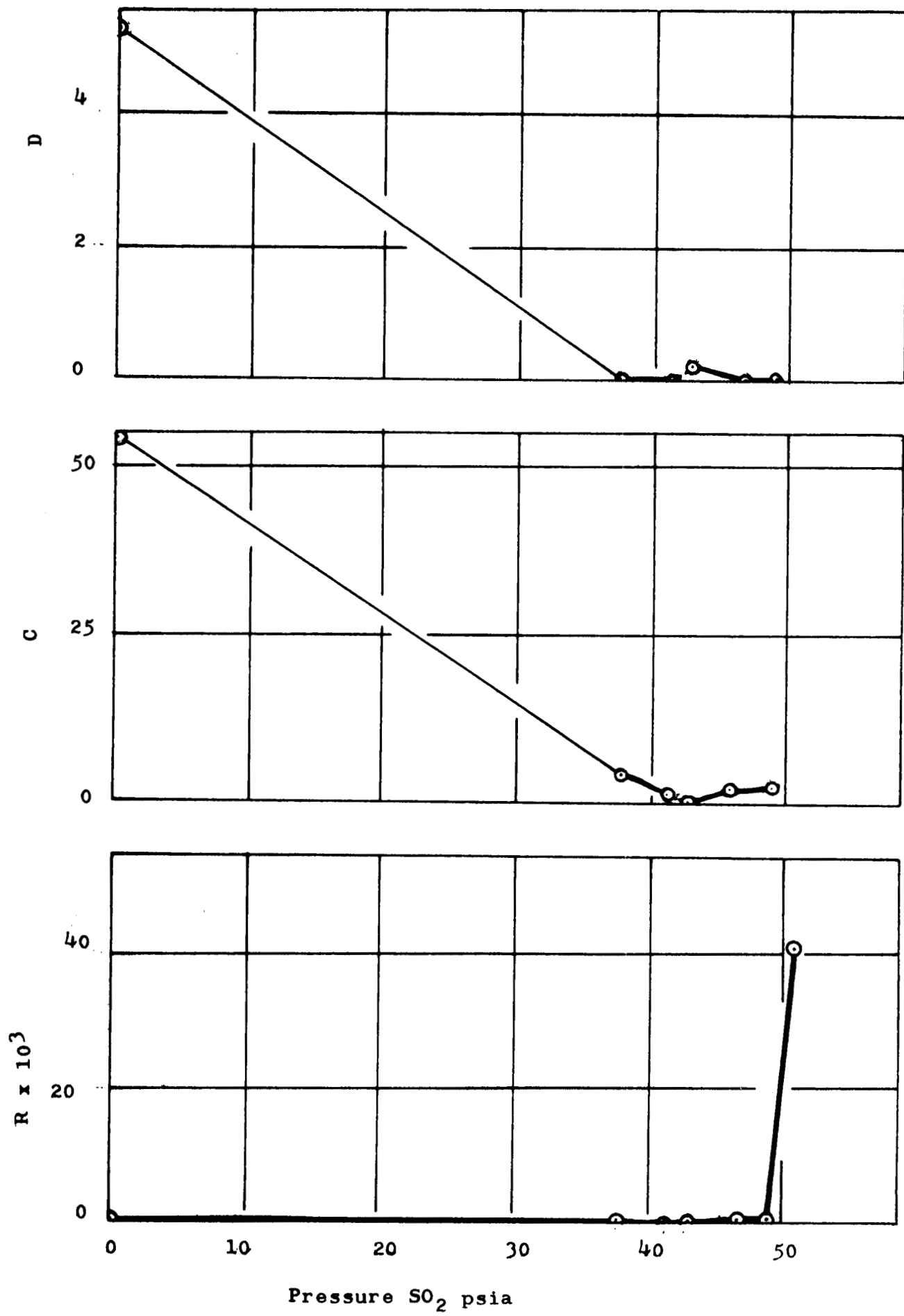
PROPYLENE CARBONATE + POTASSIUM BROMIDE



PROPYLENE CARBONATE + SODIUM IODIDE



PROPYLENE CARBONATE + TETRAMETHYL AMMONIUM CHLORIDE



PART III

THEORETICAL APPROACH TO ANODES

Appendix III provides a thermodynamic method of estimating electrode potentials in nonaqueous solvents based upon data obtained in aqueous solutions. The results obtained using this approach were well within 0.1 V of the observed values for seventeen cells in liquid ammonia.

In applying the concept of the ligand atmosphere to the battery, the coordination possibilities become potentially more complex. A competition may exist, not only between the solvent and solute for the coordinate position, but also between the atmospheric constituent and the solvent and solute. The effect of the resulting coordination upon cell voltage and reaction weight may become quite important. Competitive and augmentative reactions will be possible from the following list:

Anode Types by Coordination Pattern

1. Anode reaction product is uncoordinated by solvent, solute, or atmosphere and is probably insoluble.

Example: The anode of an aqueous lead-acid battery.

Advantage of minimum reaction equivalents though example is electrolyte limited.

2. Anode reaction product is coordinated by atmosphere. Anode potential will increase, but reaction weight must include consumed atmosphere.

Example: None available. A similarity to the Leclanche anode might be drawn.



3. Anode reaction product is coordinated by solvent. Anode potential will increase, but reaction weight will probably exceed that of two above.

Example: Most aqueous anodes.

4. Anode reaction product is coordinated by solute. Voltage and weight increase.

Example: Halide ion complex.

In view of Appendix III the contribution of the anode voltage by coordination might well be approximated by the techniques outlined. The literature of coordination compounds (via Chemical Abstracts) may yield data suitable for transformation from one solvent to another by means of the techniques of Bjerrum¹, Jolly², and Meyers³. That is, the aqueous chemical data on ligands, solutes, and solvents, will be used to derive free energy corrections for anode potentials in other solvents.

1 Journal of Chemical Reviews, 46, 381, 1950.

2 University of California Radiation Laboratory Report, UCRL-2201, May, 1963.

3 Appendix III

PART IV

BATTERY CONSTRUCTION AND TESTING

During the quarter a number of electromotive cell tests were run. The solvent oriented approach and the aim towards such couples as lithium/fluorine imply significant engineering difficulties to be overcome. The use of a glass ion exchange membrane with these anodes has been mentioned.¹ This membrane must be unusually thin so that the construction of closely spaced cells was given considerable thought. The first test vehicle is shown in Plate II, page 73. Three stable Pt/NH₃/soda lime glass anodes were fabricated despite the obvious difficulties of construction. They consisted of a platinum wire sealed into a soft glass tube partially filled with liquid ammonia and extending into a short sealed capillary. Attempts were made to electrodeposit alkali metals through the capillary walls into the ammonia. This secondary battery method was unsuccessful. The primary battery approach will next be tested using commercial glass electrodes immersed in lithium bronze, Plate III, page 74. Two appropriate glass electrodes (sodium and cationic) have been procured, and a pH meter has been calibrated to read beyond its normal range. The theoretical couple involved will be Li-NH₃//AgCl-H₂O. A comparison between the theoretical and the observed potentials for this hybrid solvent cell will be most interesting. Other glass compositions and fabricated items are being considered for their exchange properties in this application. One preliminary experiment with an organic membrane did not result in immediate destruction of the cell, and a voltage was observed. Further work along this line is indicated.

As stated previously, the solvent oriented battery equation indicated that a cell using water as a solvent should be capable of producing its maximum energy output when operated at a potential of 3.2 volts. In order to approach this high potential, the anode must be in a basic anolyte and the cathode must

¹Livingston First Quarterly Report on Page 19.

be in an acid catholyte. Under these conditions, theoretically, the anode could yield 1.3 volts; and the cathode could produce 1.7 volts for a system voltage of 3.0. The construction of a cell with these characteristics requires the use of two ion exchange membranes, a strong acid membrane, and a strong base membrane. See Plate I, page 8.

Using these principles, an aqueous cell was constructed (see Table I) and initially gave 2.9 volts open circuit potential. This cell utilized the $\text{Mg-Mg(OH)}_2/\text{HOCl}$ couple and ran for twenty hours. A second cell based upon the $\text{Mg-Mg(OH)}_2/\text{KMnO}_4$ couple gave 2.95 volts open circuit. Since potentials of sufficiently high value and stability are available, this approach warrants more detailed examination with respect to stoichiometry and electrode kinetics. See Plate IV, page 75.

During the quarter, four stainless steel pressure chambers and associated hardware were assembled to expand the testing program of low boiling solvents and to conduct cell tests under pressure.

It was deemed desirable to conduct a multiplicity of tests in each of these chambers and, thereby, risk some possibility of interaction rather than set up a large number of these relatively costly units. In cases of doubt concerning interaction of one test with another in the same chamber or with combinations of particular importance, individual repeat tests can be made.

By using existing Livingston cell holders modified as shown in Figure II, page 19 it will be possible to run six conductivity tests in each test chamber instead of one. In this new test vehicle, solder joints have been eliminated and have been replaced with Teflon covered wire. These changes have been made to eliminate corrosion and decomposition that were problems in the previous test cells.

In addition to the stainless steel pressure chamber, special glass apparatus was designed and acquired for the evaluation of ion exchange membranes and separators in half-cell testing media.

PART V

RESEARCH CELL AND SEPARATOR RESISTANCE MEASUREMENT
EQUIPMENT

The application of half-cell and reference electrode techniques in varying solvents and under various atmospheric conditions is subject to many practical and theoretical difficulties. One technique for overcoming many of these problems has been described in the Proposal and an example cited of its application to the selective study of electrodes and separators in ammonia.

The technique consists of constant average driven discharge of the cells under a cyclic loading program allowing frequent measurements of open and closed circuit voltages of the complete cell and its individual components as resolved by two reference or auxiliary unloaded electrodes. The two extra electrodes permit division of the complete cell into two half-cells and provide an index of their mutual reliability by comparison of one with the other. Frequent verification of references is necessary for sealed cells and for cells of unusual solvents. In addition, the load current may be chopped at a comparatively high frequency during the load-on half of the duty cycle to provide equally comprehensive a. c. measurements for cell component resistance evaluation. Since about 16 different measurements are required on a continuous basis, an automatic strip chart recording system is required.

Previously it was planned to set up the 12-channel strip chart recorder being used for the specific resistance and Tafel data scanning with a program board system, permitting the same recorder to be utilized for half-cell work during the daytime and the solvent scanning at night and over weekends. Now that the automatic scanning is in progress, it became apparent that there would be interference between these two programs. Many of the cells may require overnight operation, and certain

specific resistance/Tafel scans are best monitored by the operators. In addition, some down-time would be required in the revision of the circuitry for both operations.

A schematic diagram of the approach now formulated for this work is given in Figure VII, page 63. The symbols E_1 , E_2 , etc. refer to the various automatic recorder functions listed in Table III, page 64. An additional color-coded strip chart recorder will be used for this application. The ten-inch strip chart will be divided into two halves by appropriate bias, and the zero to five volts d.c. scales will be displayed to the right allowing a similar span for monitoring half cells which fail while the remaining half-cell data is collected. A.c. voltages, pressure, and cell current will be displayed starting at the extreme left minimizing intermingling of the 16 curves to be traced.

Concerning the cell discharge load current wave form, two frequencies are of basic importance. First is the basic on-off repetition rate. It is planned to use a value in the order of thirty seconds, i.e., fifteen seconds on fifteen seconds off. Each of the four cell terminal combinations will be scanned at the end of a load-on half-cycle and at the end of a load-off half-cycle. The load pattern will therefore be orthogonal; and each reading will have a comparable history. The average load current over the entire on-off cycle will be one half of the value for the fifty percent on-period. The load-on period will also be interrupted, but at a higher repetition rate to retain polarization loss during the short, but repetitive off-periods of the basic load-on period. The load-off sub-periods will be of relatively short duration compared to the load-on sub-period.

The current-regulator system will be of relatively high impedance so as to hold the load current pulses relatively square and at a fixed peak and average value. The schematic Figure VIII on page 65 shows the general approach which will be used in constructing the current regulator system. This schematic is annotated with wave forms. The operation of the system will be more apparent from a study of the circuit. The sixty cycle sine

input of the line power will be stabilized and converted to a fairly sharp square wave by the saturable reactor type voltage regulation transformer. The pentode control tubes will rectify and limit the cell current to the desired setting. The short, but definite, off sub-periods of the on-cycle result from the full wave rectifications of the square wave voltage applied to the plates. It is anticipated that this short off-period will substantially discriminate between electromotive cell resistance and polarization effects.

Most of the major components of this system including the twenty-six point external scanning switch and color-coded electronic strip chart are now in stock at Montgomeryville.

SCHEMATIC DIAGRAM OF MULTIPLE RECORDING
SYSTEM TO FACILITATE 1/2 CELL STUDIES IN VARIOUS
MEDIA

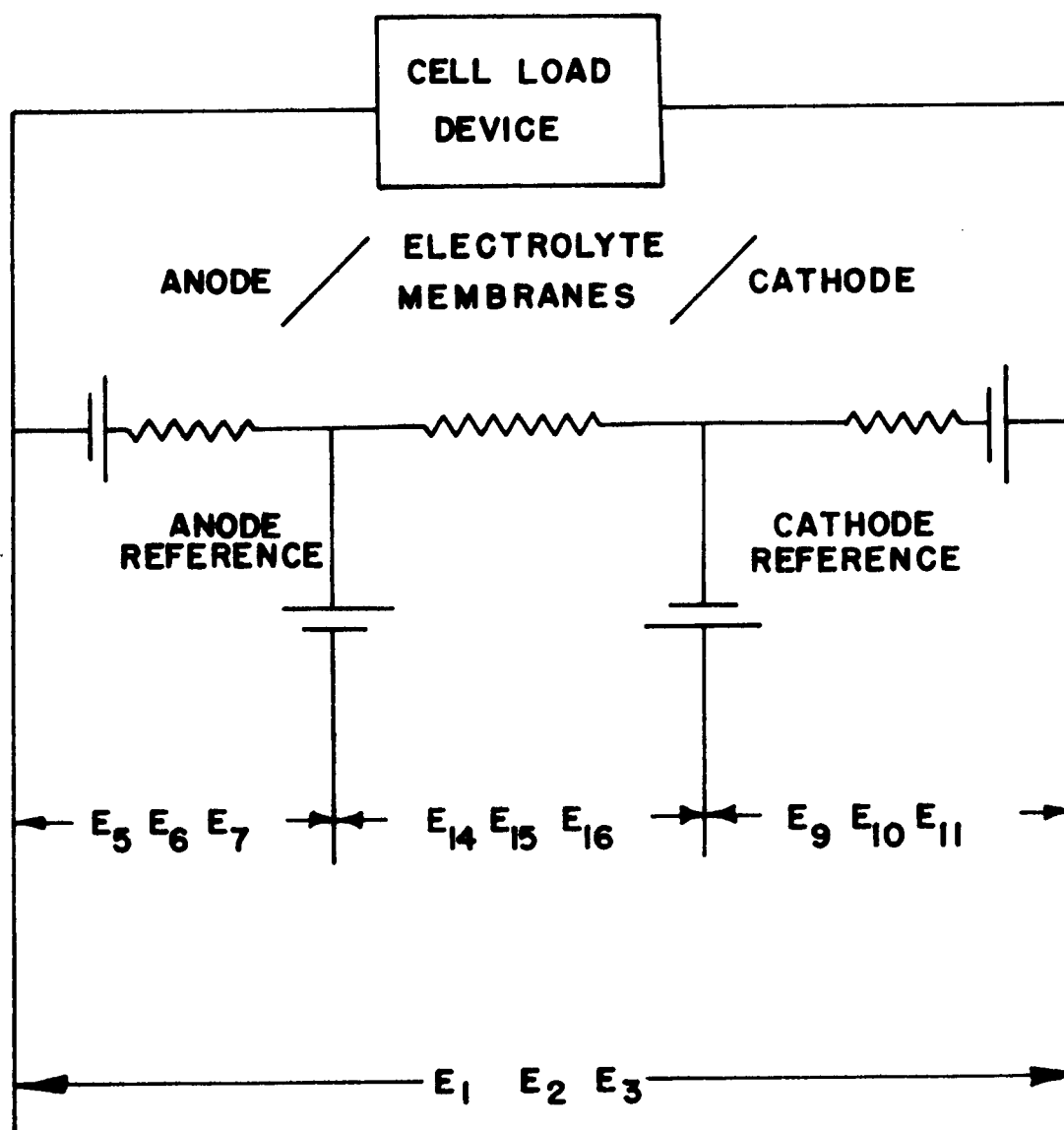


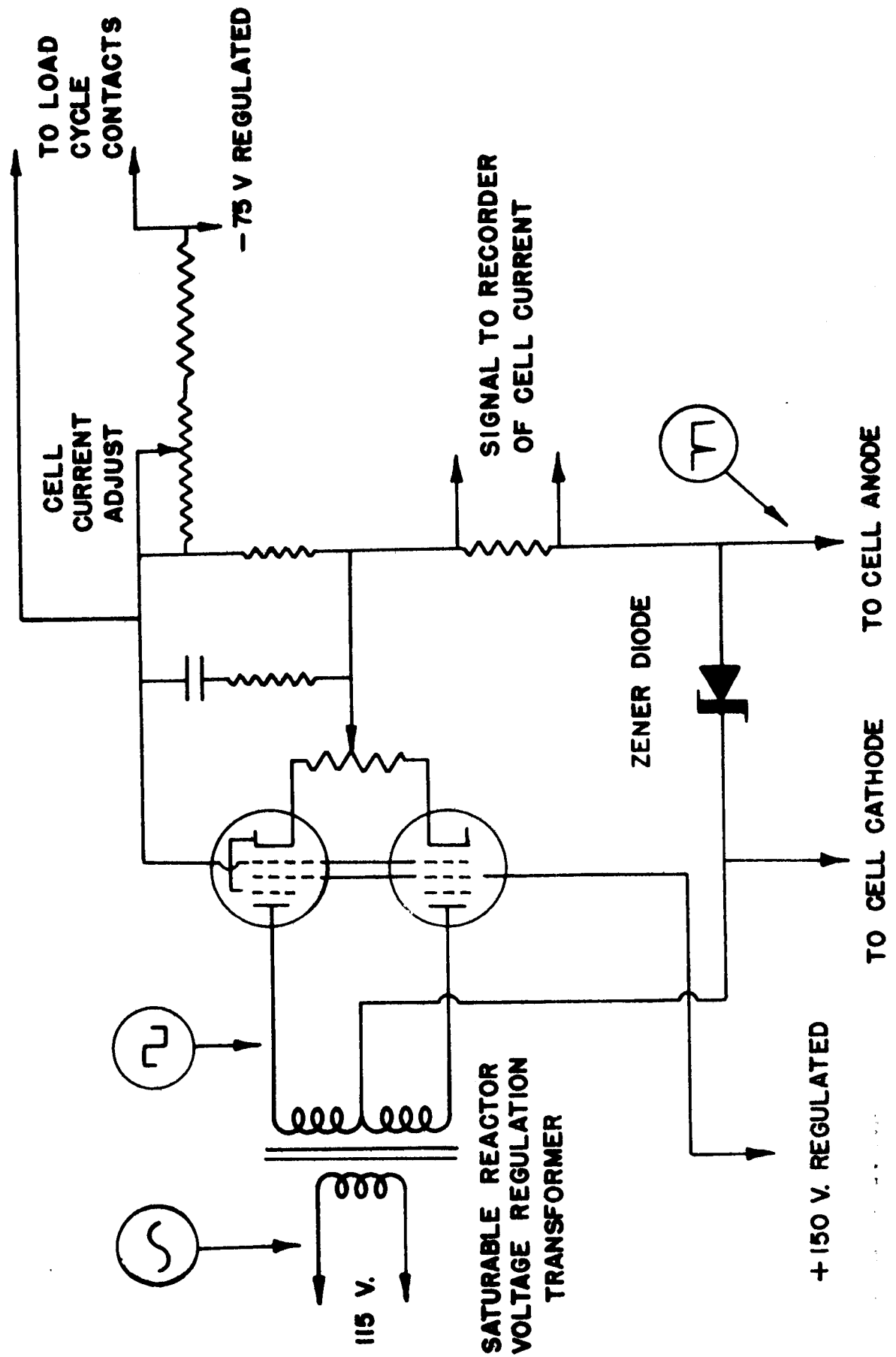
TABLE III
Research Cell Recorder Functions

Scanner Position	Recorder Channel	Load	Zero Location	Color Code (a)	Scale Type	Signal Source
1	1	+	$\frac{1}{2}$	R	d. c.	Cell
2	2		$\frac{1}{2}$	R	d. c.	Cell
3	3	+	0	R	a. c.	Cell
4	4		0	P	a. c.	Pressure
5	5	+	$\frac{1}{2}$	G	d. c.	Anode
6	6		$\frac{1}{2}$	G	d. c.	Anode
7	7	+	0	G	a. c.	Anode
8	8		0	R	a. c.	Pressure
9	9	+	$\frac{1}{2}$	P	d. c.	Cathode
10	10		$\frac{1}{2}$	P	d. c.	Cathode
11	11	+	0	P	a. c.	Cathode
12	12					Reserved
13	1	+	$\frac{1}{2}$	G	d. c.	Cell
14	2		$\frac{1}{2}$	G	d. c.	Cell
15	3	+	0	G	a. c.	Cell
16	13					Reserved
17	14	+	$\frac{1}{2}$	R	d. c.	Electrolyte
18	15		$\frac{1}{2}$	R	d. c.	Electrolyte
19	16	+	0	R	a. c.	Electrolyte
20	17					Reserved
21	18	+	0	G	a. c.	Current
22	19					Reserved
23	20	+	0	P	a. c.	Current
24	21					Reserved
25	22	+				Reserved
26	23					Reserved

(a) R = red, G = green, P = purple

FIGURE VIII

LOAD CURRENT REGULATOR AND CHOPPER SCHEMATIC



PART VI
MATERIAL TESTING

The chemical stability and corrosion resistance of ion exchange membranes, separator materials, and materials of construction (alloys, metals, polymers, resins, paper, and fibers) were determined in non-aqueous solvents and in selected environments which were composed of solvent, salt, and ligand. The selected environment represents the media in which these materials must exist during operation and storage. The severity of corrosion effects and decrease in chemical stability with time may be attributed to the synergistic action of the ligand (SO_2 , NH_3 , etc.) and the anion (Cl^- , F^- , Br^- , etc.) resulting from the dissociation of the salt.

The performance of the specimens were determined by periodic inspection. Evaluation of the alloys and metals were based on the pitting, blistering, cracking, discoloration, crazing, and other changes in appearance that resulted from corrosion of the specimens. Objective evaluations of the ion exchange membranes and separator materials were based on change in appearance, dulling, swelling, discoloration, dissolution, and degrees of deterioration.

The Nylon and Teflon conductivity cells have apparently withstood the combined effects of various solvents, solutes, and three types of atmospheres (air, SO_2 and NH_3) without general damage. As the work proceeds towards construction of batteries other practical materials of construction will require evaluation under these combined deteriorating conditions.

The conditions generated within the pressure chambers for the automatic recording of electrolyte specific resistance and Tafel data will combine the factors which may decompose or corrode materials of construction; thus, pressure chambers can conveniently include samples for exposure.

In order to accomplish this, the new polypropylene cell holders have been employed as containers for materials testing by charging them with various solvent/solute combinations, after which samples of numerous

materials of construction, ion exchange membranes, and separators have been placed in the cells. The charged cells were then placed in the stainless steel chambers, and gas pressure was applied and maintained for the duration of the tests. See Tables IV and V, pages 68 and 70.

At the conclusion of the test period, the pressure was released and the samples were removed from the cells and examined for physical and chemical changes caused by the exposures.

Secondary results from the conductivity tests show that in cell tests involving NH_3 at pressures from zero to one hundred and twenty psi, the tin-plated copper wire would eventually corrode to such a great extent as to become powdered. The same was true for the solder connections which are sixty percent tin, forty percent lead. Apparently, ammonia will attack both tin and copper, and to such a degree as to powder both wires and solder containing these elements. The platinum wire was not affected.

In the cell tests, using sulfur dioxide at pressures from zero to forty psi, the polypropylene cells swelled and became discolored. When they were cleaned and dried in a vacuum oven after use, both of these effects disappeared.

As for the tin-plated copper wire, it was attacked by sulfur dioxide as it was by ammonia with much the same effects. Tin/lead solder was not employed, but instead nickel-plated copper clips were used. After one test run, the nickel plating was completely gone, and the attack on the copper had already started. The platinum and the silver wires apparently were unaffected.

Table No. IV is a summary of the results obtained from exposure of materials to solvents alone. Table V shows the combined effects of propylene carbonate solutions in the presence of SO_2 at 32 psig.

TABLE NO. 17

CODE:

Compatibility of Materials in Various Solvents

IE = Ion Exchanger S = Separator n = Nylon a = Dynel l = Cellulose i = Impregnated paper pp = polypropylene v = Viscose c = Cotton			"C" = Compatible "I" = Incompatible "Q" = Questionable										
			SOLVENTS	Liquid Ammonia	Isopropylamine	Freon #11	Freon #113	Propylamine	Acetone	Ethyl Acetate	Triallylamine	N, N-Dimethyl-Formamide	Petroleum Ether
DAYS UNDER TEST:				5	5	4	6	5	4	4	4	4	4
SB 6407	IE	n		C	C	C	C	C					
WA 6402	IE	n			C	C	C	C					
WB 6403	IE	n		I	C	C	C	C					
SA 6404	IE	n			C	C	C	C	C	C	C	I	C
WA 6406	IE	v			C	C	C	C					
XLMC 3235	IE	-							I	I	C	I	C
XLMA 3236	IE	-							I	I	C	I	C
ET 20	IE	-		I					C	C	C	C	C
AE 30	IE	-		I					C	C	C	C	C
DE 20	IE	-		C					C	C	C	C	C
P 20	IE	-		I					C	C	C	C	C
CM 50	IE	-		I					C	C	C	C	C
Whatman 42	S	l		C	C	C	C	C	C	C	C	C	C
M 1401	S	a		I	C	C	C	C	I	C	C	I	C
EM 312	S	n		I	C	C	C	C	I	C	C	Q	C
M 1216	S	v			C	C	C	I					
M 1231	S	v		C	I	C	C	C	C	C	C	C	C
EM 478	S	v		C	C	C	C	I					
M 1365	S	c			I	C	C	I	C	C	C	Q	C
EM 476	S	pp			C	C	C	C	C	C	C	C	C
R 2205	S	l			C	C	C	C	C	C	C	C	C
Polyethylene	S	-			C	C	C	C	C	C	C	C	C
Ultipor 9	S	i		I	I	C	C	I					
Epocel 10	S	i		C	C	C	C	C					
PC 1478	S	i		C	C	C	C	C					
EM 470	S	a		I									
M 1410	S	a		I									
M 1450	S	a		I									
M 1406	S	n		C									

In reference to Table IV, the materials that did not fail in any of the solvents in which they were tested are: The Gelman ion-exchange membranes SB 6407, WA 6402, WA 6406; Whatman #42 filter paper; polypropylene (EM 476); R-2205 (Cellulose); polyethylene; Epocel 10; IPC 1478; the Whatman ion-exchange membrane DE 20; and M 1406 (Nylon).

Those which failed in one solvent only are: Gelman ion-exchangers WB 6403 and SA 6404; M 1216 (viscose); M 1231 (viscose); EM 478 (viscose); the Whatman ion-exchangers ET 20, AE 30, P 20 and CM 50; and the dynel fabrics EM 470, M 1410, and M 1450.

The solvents which did not exhibit destructive action on any of the materials tested are: Freon 11, Freon 113, triallylamine and petroleum ether.

In liquid ammonia, all of the dynel fabrics shrank from 1/2" x 1-1/8" to 1/8" x 3/8".

Viscose and paper held up well. However, the ion exchange material in WB 6403 was partially removed from the Nylon and Ultipor 9 seemed to have suffered from decomposition.

TABLE V
MATERIALS COMPATIBILITY TEST RESULTS
PROPYLENE CARBONATE, SO₂, AND VARIOUS SOLUTES

Sulfur Dioxide Atmosphere		32 P.S.I.G. and		Room Temperature		
Solute		None	AlCl ₃	LiCl	LiF	KBr
Days Under Test		2	5	5	5	5
Material						
SA 6404	IE	-	Q	I	Q	Q
MC 3142	IE	-	Q	Q	Q	Q
MA 3148	IE	-	Q	Q	Q	Q
XLMC 3235	IE	-	Q	Q	Q	Q
XLMA 3236	IE	-	Q	Q	Q	Q
ET 20 Anion	IE	-	Q	C	Q	Q
AE 30 Anion	IE	-	Q	Q	-	-
DE 20 Anion	IE	-	Q	Q	-	-
P 20 Cation	IE	-	Q	C	Q	Q
CM 50 Cation	IE	-	Q	Q	-	-
Whatman 42	S	C	-	C	C	C
M 1216	S	C	-	C	C	C
M 1231	S	C	-	C	C	C
EM 478	S	C	-	-	-	-
M 1365	S	C	-	C	C	C
EM 476	S	C	-	-	-	-
Polypropylene						
Cell	M	-	C	C	C	C
R 2205	S	C	-	C	C	C
Polyethylene	SM	C	-	C	C	C
Ultipor 9	S	C	-	-	-	-
Epocel 10	S	C	-	-	-	-
IPC 1478	S	C	-	-	-	-
Nalco D 30	S	-	I	I	I	I
Aluminum	M	-	C	C	C	C
Stainless steel	M	-	C	-	-	-

Code: "C" = Compatible, "I" = Incompatible, "Q" = Questionable, "IE" = Ion Exchange Membrane, "S" = Separator Material, "M" = Material of Construction.

The use of "Q" to describe the results of most of the tests on ion exchange membranes indicates that the membranes appeared to be unaffected. However, the effects, if any, on the ion exchange resin cannot be determined with certainty by inspection. The efficiency of the resins as ion exchangers may be determined best by testing them in battery cells.

Most of the ion exchange membranes listed in Table V appeared to withstand the exposures very well. All of the separators and materials of construction which were checked in this series of tests were found to be satisfactory, except that Nalco D-30 was dissolved by propylene carbonate.

PART VII

WORK TO BE PERFORMED DURING THE NEXT PERIOD

I. During the Next Quarter

The production of specific resistance/Tafel data will continue, and the number of simultaneously recorded cells will be increased to nine channels. Greater theoretical consideration will be given to the compatibility of the solvent-atmosphere combinations selected for test. This will be based in part upon results obtained.

The research cell recording equipment outlined in this report will be constructed early in the next quarter, and a fund of data is anticipated by the end of the quarter.

The theoretical aspect of electrode potentials in solvent-solute-atmospheres will be considered from the standpoint of generalization.

The next phase of the material testing program will consider the effect of swelling of the ion exchange membranes on capacity, electrochemical properties, and sorption equilibria in non-aqueous solvent-salt-ligand media. Ion-exchange and sorption equilibrium depend strongly on the nature of the solvent. The most important factors which will determine the equilibria and selectivities are dissociation and solvation in these solvents and specific interactions such as a complex formation. A change of solvent may result in striking changes in selectivity, particularly if specific interactions are involved.

The task of building batteries, which will utilize Livingston hardware, has been assigned to a newly organized group under the guidance of an experienced junior engineer. The technicians for the group were drawn from teams producing batteries and hardware of the types involved. An additional area adjacent to the initial facility has been assigned for testing and producing these non-aqueous batteries.

II. During the Next Month

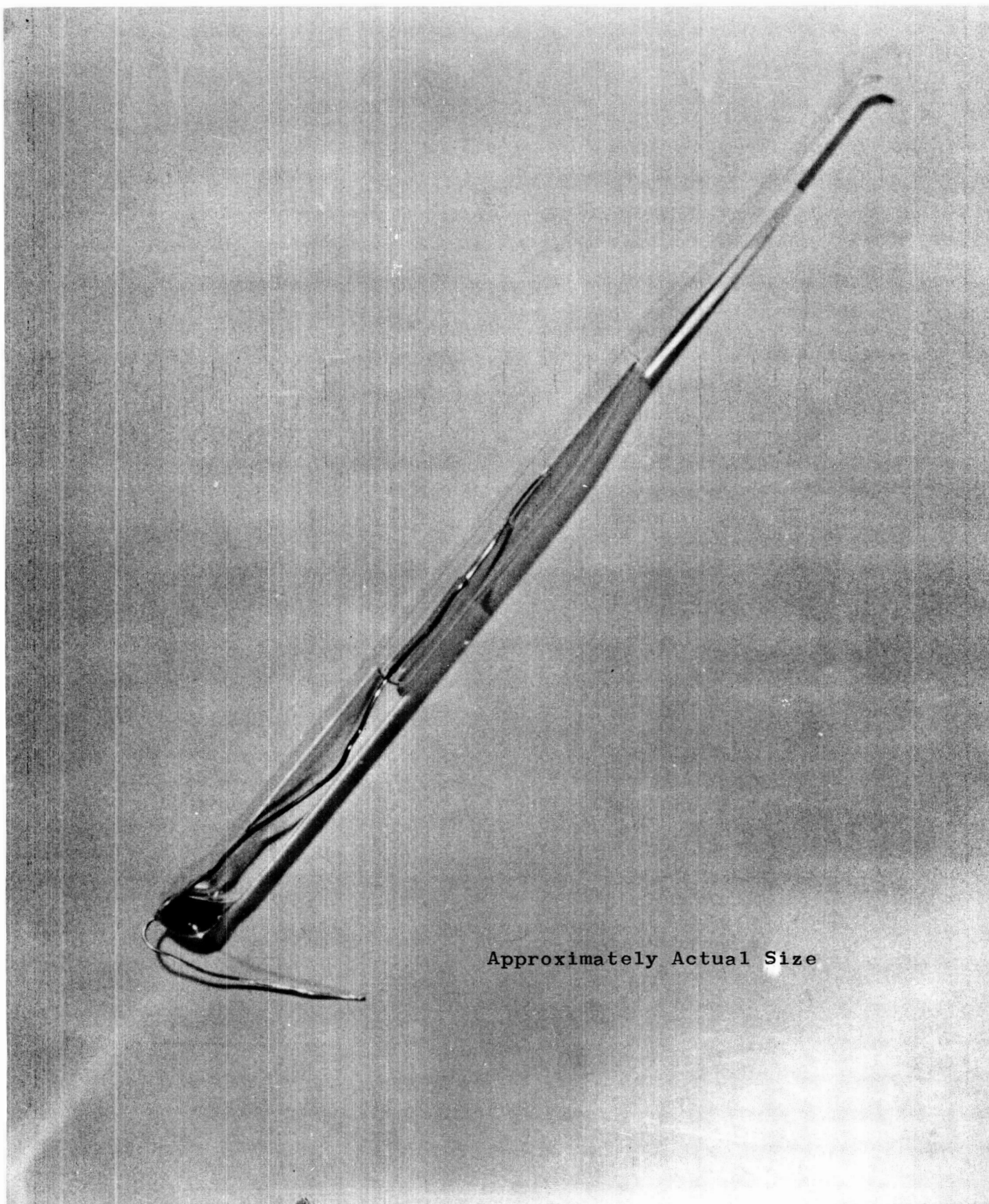
Construction of the nine-channel secondary scanning system for the specific resistance/Tafel data will be actively pursued. A few minor circuit modifications will be introduced to extend the range of the data, simplify calculations, and to help explain anomalies arising in certain combinations.

Improved methods of handling the thousands of raw data points into R, C, and D values will be studied. The data included in this report was obtained by selecting approximately one scanning cycle out of ten recorded on the charts.

Now that the solvent theory and scanning are underway, greater effort will be directed towards research cells and practical cells in existing Livingston Ammonia Battery vehicles. Additional personnel will be assigned to augment those presently engaged in this work.

-73-

PLATE I



Approximately Actual Size

Lithium Bronze Anode Vehicle

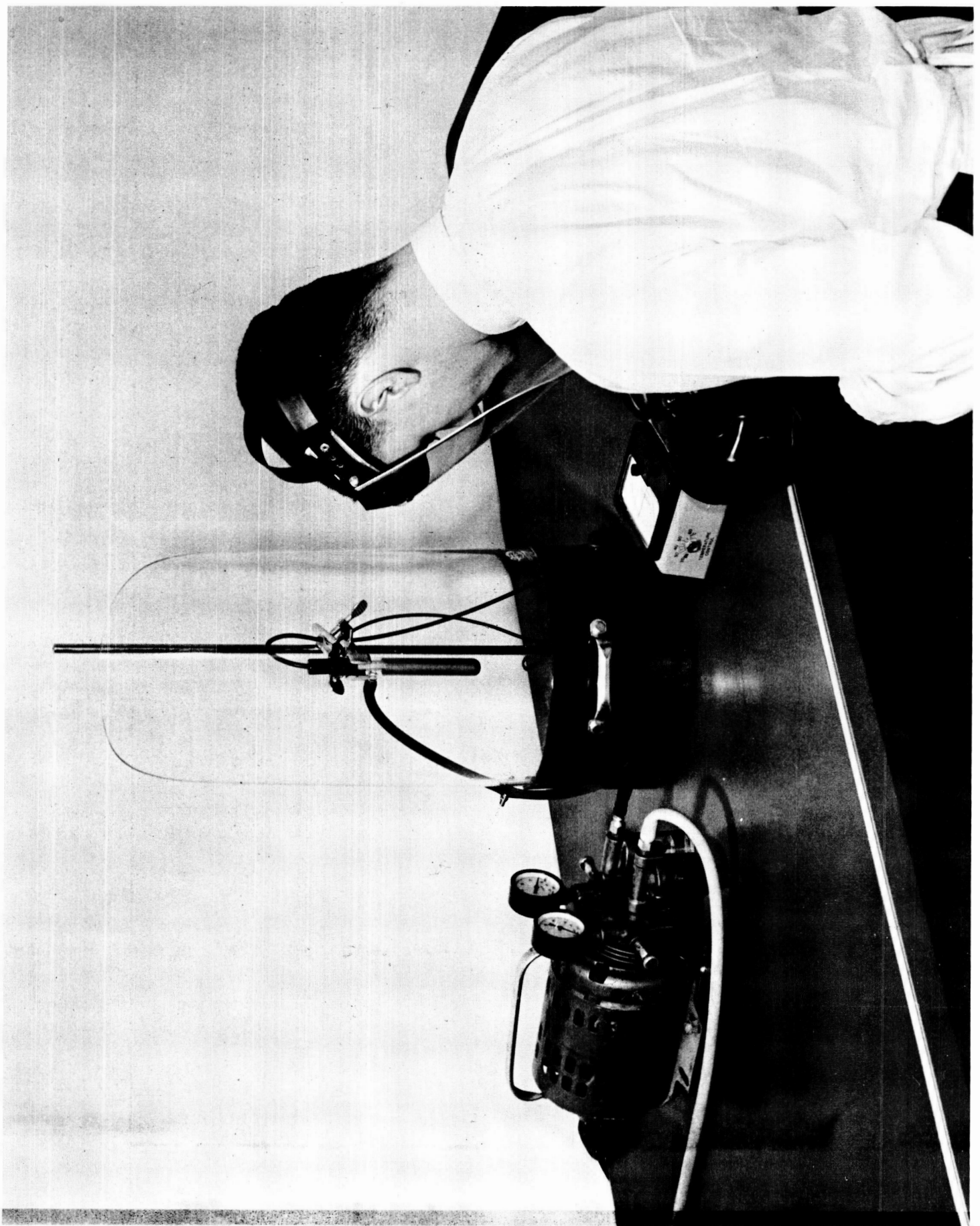


PLATE III

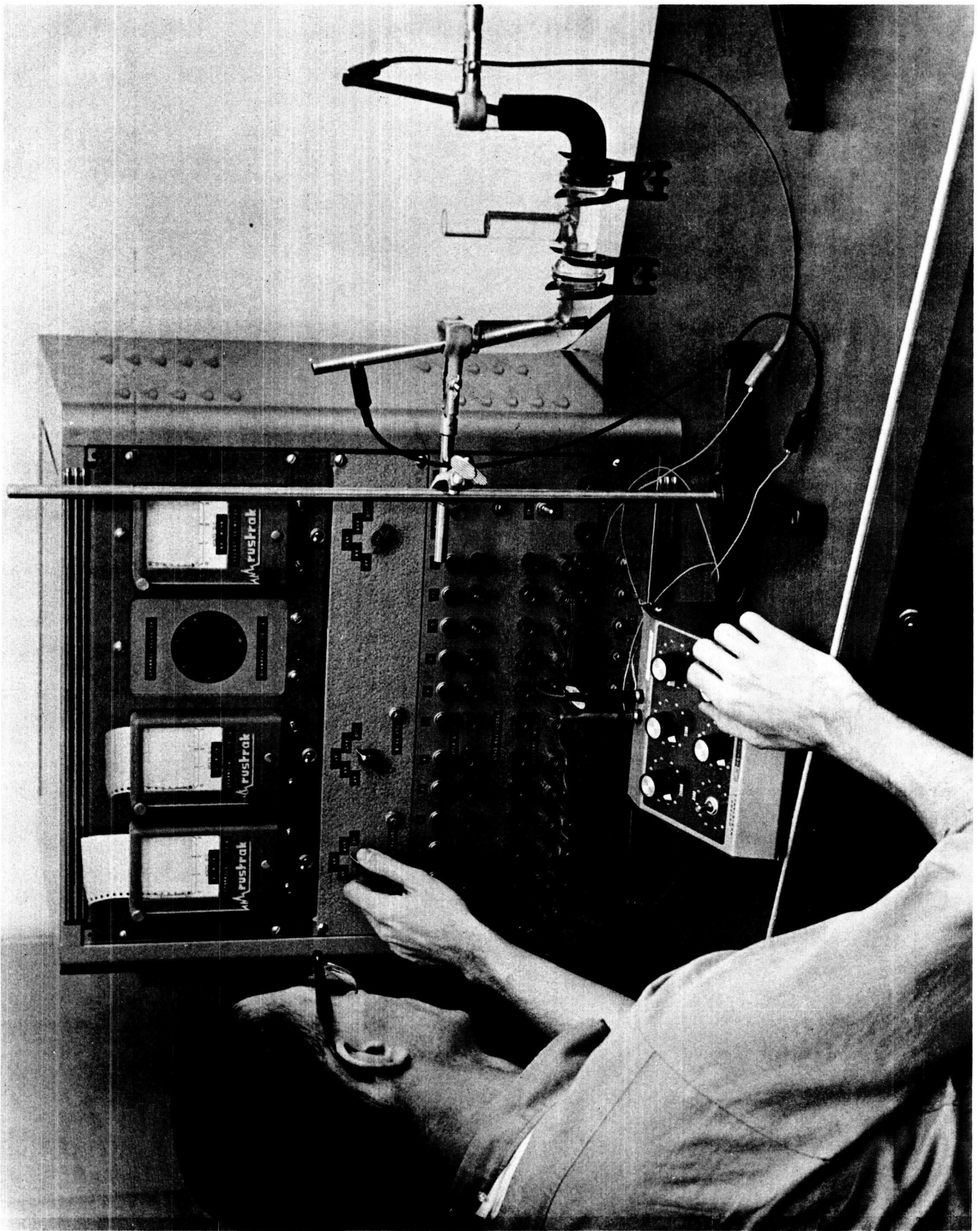


PLATE IV

Reference I

Log of Report Numbers

Card
Col.

		Report On:	Column 3 Code Entry 2
4 5 6			
1 3 8		"Basic Studies on Fuel Cell System " Electrochemistry Research Lab., Lockheed Missiles and Space Co., Sunnyvale, California, M. Eisenberg, ASTIA, AD 298,768.	
1 3 9		"New Cathode-Anode Couples Using Nonaqueous Electrolyte, " Electrochemistry Lab., Lockheed Missiles and Space Co., ASTIA, AD 401,846.	
1 4 0		"Electrochemical Mechanism of Metal Corrosion Influenced by Alternating Current. II. Dissolution of Lead on Polarization with Alternating Current, " English Abstracts of Selected Articles from the Soviet Bloc and China, Series II, September, 1963.	
1 4 1		"High Purification of Lithium by Elution Chromatography, " Eng. Abs. of Sel. Articles, Series II, September, 1963, <u>ibid.</u>	
1 4 2		"Some Laws Relating to the Electrolytic Deposition of Alloys, " Eng. Abs. of Sel. Articles, Series II, September, 1963, <u>ibid.</u>	
1 4 3		"Corrosion of Apparatus During the Production of Potassium by the Alkali Method, " Eng. Abs. of Sel. Articles, Series II, September, 1963, <u>ibid.</u>	
1 4 4		"Configuration Index for the Electron Structure of Normal Atoms, " Eng. Abs. of Sel. Articles, Series II, September, 1963, <u>ibid.</u>	
1 4 5		"Calculation of the Stability Constants for Polyiodide Anions in Nitrobenzene, " Eng. Abs. of Sel. Articles, Series II, September, 1963, <u>ibid.</u>	
1 4 6		"Investigation of the Kinetics of the Thermal Decomposition of Ethane with a Single-Pulse Shock Tube, " Eng. Abs. of Sel. Articles, Series II, September, 1963, <u>ibid.</u>	
1 4 7		"Sorption of Phenols by Ion Exchange Resins, " Eng. Abs. of Sel. Articles, Series II, September, 1963, <u>ibid.</u>	

Log of Report Numbers

Card
Col.

		Report On:	Column 3 Code Entry 2
1	4 8	"Structure and Adsorption Properties of CaA-Zeolites Having Cation Exchanged Forms," Eng. Abs. of Sel. Arts., Series II, September, 1963, <u>ibid.</u>	
1	4 9	"Electrical Conductivity and Activation Energy of Chelate Compounds of the Dithiocarbonates and Thicamides of Pyridine Derivatives," Eng. Abs. of Sel. Articles, Series II, September, 1963, <u>ibid.</u>	
1	5 1	"Importance of the Structure and Physical State of Extraction-Solvent Molecules," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1	5 2	"Absorbing Characteristics of Surfactants at the Electrode-Solution Boundary," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1	5 3	"The Effect of the Movement of a Solution on the Purity of the Obtained Crystals," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1	5 4	"New Method of Synthesizing Amine Borine and its Properties," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1	5 5	"The Investigation of Complex Formation Between Uranyl-Ion and Orthophosphoric Acid," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1	5 7	"Method of Producing Organic Substances Having the Properties of Electric Semiconductors," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1	5 8	"The Effects of Ions on the Properties of Ammoniacal Silver Bromide Emulsions," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1	5 9	"Thermal Conductivity of Organic Liquids as a Function of Pressure," Ang. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	3.

Log of Report Numbers

Card
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		Report On:	Card Column 3 Code Entry 2
4 5 6	0	"The Effect of Chlorine Ions on the Kinetics of the Cathodic Deposition of an Iron-Nickel Alloy," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1 6 1	1	"Adhesion of Electrolytic Coatings to an Electronegative Base," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1 6 2	2	"Preparation of Freon Oil -12(KhF-12) from Anastasiyevka Crude," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1 6 3	3	"The Viscosity of Aqueous Solutions of Mineral Salts," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1 6 4	4	"X-Ray Examination of the Structure of Na-Borate Glasses," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1 6 5	5	"The Structure of Silicate Glasses and the Formation of Aluminum Phosphate Glasses," Eng. Abs. of Sel. Articles, Series II, August, 1963, <u>ibid.</u>	
1 6 6	6	"Theory of the Electric Interaction of Identical Discretely Charged Planar Surfaces Separated by Electrolyte Solution," Chem. Abs., Vol. 59, No. 8, 8353a.	
1 6 7	7	"Activity Coefficients of HBr from E.M.F. Measurements," CA, Vol. 59, No. 8, 8353b.	
1 6 8	8	"Solion Electrochemical Devices," CA, Vol. 59, No. 8, 8356f.	
1 6 9	9	"Process for Plating on Thin Wires," CA, Vol. 59, No. 8, 8357f.	
1 7 0	0	"Absolute Temperature Coefficient of an Electrode in Any Solvent," CA, Vol. 59, No. 8, 8358a.	

Log of Report Numbers

Card
Col.

4 5 6 Report On:

Column 3 Code Entry 2

1 7 1 "Theory of the Porous Gas Electrode. Calculation of the Effective Coefficients," CA, Vol. 59, No. 8, 8358f.

1 7 2 "On the Possibility of Using Platinum-Titanium Anodes in the Chlorine Industry," CA, Vol. 59, No. 8, 8360e.

1 7 3 "Relation of the Current Efficiency in Electrolytic Production of Aluminum to the Composition of Anodic Gases," CA, Vol. 59, No. 8, 8360g.

1 7 4 "Determination of Characteristics of the Process of Electrolytic Production of Aluminum by the Composition of the Anode Gases," CA, Vol. 59, No. 8, 8361a.

1 7 5 "Comparison of Polarographic Half-Wave Potentials in Nitriles, Acetone, and Water as Solvents," CA, Vol. 59, No. 8, 8361f.

1 7 6 "The Use of Alternating Current in the Study of Polarographic Discharges," CA, Vol. 59, No. 8, 8362h.

1 7 7 "Diffusion Electrodes," CA, Vol. 59, No. 8, 8363g.

1 7 8 "Carbon of Low Electrical Resistance," CA, Vol. 59, No. 8, 8380d.

Reference II

1. "Physical Properties of Chemical Compounds", Advances in Chemistry, Series No. 15.
2. "Physical Properties of Chemical Compounds-II", 1959, Advances in Chemistry, Series No. 22.
3. "Physical Properties of Chemical Compounds-III", 1961, by Driesbach of Dow Chemical Co., Advances in Chemistry, Series No. 29.
4. "Thermodynamic Properties of the Elements", 1956, Advances in Chemistry, Series No. 18.
5. "Inorganic Reactions in Liquid Ammonia", Vol. I, Part I, 1963, by Jander, Interscience Publishers.
6. "Organic Reactions in Liquid Ammonia", Vol. I, Part II, 1963, by Herchel Smith, Interscience Publishers.
7. "Selected Values of Chemical Thermodynamic Properties-Part I-Tables", NBS Circ. 500.
8. "Selected Values of Chemical Thermodynamic Properties-Part II-References", NBS Circ. 500.
9. "Dowex Ion Exchange", 1958, 1959-The Dow Chemical Co.
10. "Chemical Trade Names and Commercial Synonyms", 2nd Edition, 1955, by Haynes, D. Van Nostrand Co., Inc.
11. "Chemical Engineers' Handbook", 4th Edition, 1963, by Perry, Chilton, and Kirkpatrick.

Reference III
Technical Bulletins and Papers

The following technical bulletins and papers have been received:

"Analysis of Theoretical Liquid Metal Cell for Energy Storage in Space"- by Heitbrink and Karas - Copied from General Motors Engineering Journal 10, No. 1, 21-5, 1963.

"IUPAC Conventions Concerning the Signs of Electromotive Forces and Electrode Potentials"- Adopted 1953 - Obtained through the National Bureau of Standards.

"Duclite Ion Exchange Manual"- Diamond Alkali Company.

"Free Fluorocarbons"- Technical Booklet - Du Pont.

"Sulfur Hexafluoride"- Technical Bulletin - Baker & Adamson.

"Matheson Gas Data Book"- The Matheson Company, Inc.

"Fluorine Chemistry"- (Reprint) - A. C. S. Applied Publications.

"Fluoro-Organics"- 3FK, 4FK, 5FK and 6FK - General Chemical Division, Allied Chemical Corporation.

"Lithium Fact File"- Foch Mineral Company.

"Lithium Organics"- Lithium Corporation of America.

"Bulletin 5009"- 38 Ion Exchange Materials - Pfaunder Permutit Inc., Permutit Division.

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"Table of Dielectric Constants of Pure Liquids"- by Maryott & Smith, National Bureau of Standards Circular 514, 1951.

"Chemical Abstracts, Applied Chemistry Sections 15 through 30", 1963.

"Nuclear Relaxation in Molecular Liquids Containing Free Radicals", Technical Report No. 61, February 26, 1963, by Gutowsky and Tai, University of Illinois, ASTIA #AD 299-427.

"Effect of the Ligand Field on the Oxidation-Reduction Properties of Compounds of the Transition Elements", by K. B. Yatsimirskii-Zh. Neorgan. Khim. 8, 876-81, 1963 (Photocopy).

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"Aluminum Fluoride Anhydrous", Olin-Mathieson Chemical Corporation, November, 1963.

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"Ion Exchange Materials", Bio-Rad Laboratories, (with 318 References).

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"Nialk Trichlorethylene", Hooker Chemical Corporation, Bulletin 44-A.

"Dimethyl Sulfoxide", Crown Zellerbach Corporation, Product Information Bulletin-No. 326-6, February, 1963. Technical Bulletin with 85 References.

"Lithium Fact File", Foote Mineral Company, Bulletins 103, 107, 109, 102, 102.1, 101, 110, 101.1, 104, 105, 106, 112, 113.

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"Benzotrifluoride Derivatives", Technical Data Sheets, Maumee Chemical Company.

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Analytical Procedures", Brochures on Aluminum Alkyls, Texas Alkyls, Inc.

APPENDIX I

Deliberation on the high equivalent weight and low voltage of aqueous batteries leads to the realization that a limiting approximate relationship exists between oxidation potential and equivalent weight. In Table I of this Appendix some examples of conventional or desirable anode reactants are listed with their equivalent weights and acid aqueous electrode potentials. Figure I is a semi log plot of this data with the equivalent along the log axis. Note that lithium represents a limiting case for the alkali metal family, and the points for K and Na are rejected in this derivation. Mg represents the limiting case for the alkaline earths. A line is drawn through the remaining points of Figure I representing mathematically the approximate anode equivalent weight as a function of anode potential.

Cathode reactants were similarly treated, and the two lines combined. The equation $M = e^{(S - HX)}$ was abstracted from the plots where M is equivalent weight, X is the electrode potential, and S and H are characterizing constants.

The correct values for S and H were found to be approximately 5.5 and 0.4 respectively.

More comprehensive plotting and numerical regression of the line to the points would be expected to provide additional significant figures, but the above appear adequate for selection and screening of solvents.

NOTE: Appreciation is expressed to Mr. William A. Robertson of NASA for early detection and correction of an error made in the reasoning used to abstract the one equation from the two plots.

TABLE I
OF APPENDIX I

Elements	Equivalent Weight	Acid Aqueous Oxidation Potential E° (Volts)
Li	7	+3.0
Na	23	+2.7
K	39	+2.9
Mg	12	+2.4
Ca	20	+2.9
Al	9	+1.7
Be	4.5	+1.85
Zn	33	+0.8
Cd	56	+0.4
Pb	104	+0.1

AQUEOUS OXIDATION POTENTIALS vs. STANDARD HYDROGEN ELECTRODE
APPENDIX I - FIGURE I

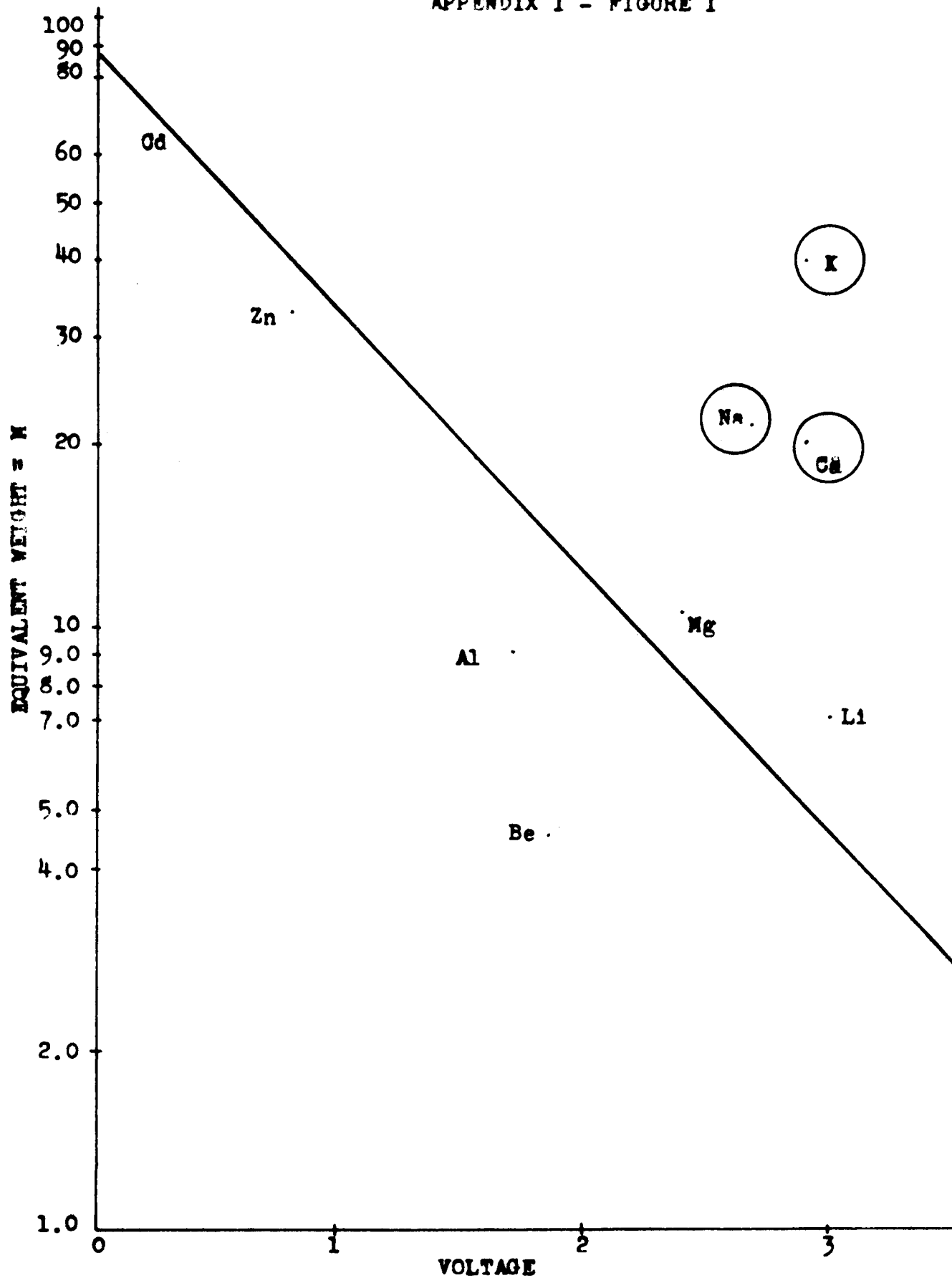


FIGURE III

APPENDIX II

This appendix illustrates one path whereby the Tafel equation ¹.

$$\eta = a + b \log i \quad (1)$$

may be modified to generalize the corrosion current of batteries which may be constructed using a wide variety of solvents. The terms of this equation (1) normally are restricted to one electrode and do not include the initial reaction standard potential nor the effects of concentrations upon reaction potential:

$$\begin{aligned} \eta &= \text{overvoltage (volts)} \\ a &= \text{the Tafel constant (volts)} \\ b &= \text{the Tafel slope (volts)} \end{aligned}$$

Battery local action may be characterized by a single equation of the same form when the terms are conveniently chosen. This equation may then be rearranged to yield a theoretical value for battery local action current density as an explicit function of battery potential in terms of conveniently measured parameters of the solvent-atmosphere combination:

$$J = e^{(X-C)/D} \quad (2)$$

Starting with a generalized solvent autoionization reaction (3) applicable to most solvents:



The voltages required to decompose the solvent AB by the physical model of Figure III on page 20 using a neutral solute of high decomposition potential is given by equations (4) and (5)^{2,3}. Equation (4) treats battery anode local action and (5) battery cathode local action.

$$E_1 = E_1^\circ - \frac{rt}{NF} \ln \frac{[A^+]}{[AB]} + \eta_1 \quad (4)$$

$$E_2 = E_2^\circ + \frac{rt}{NF} \ln \frac{[B^-]}{[AB]} - \eta_2 \quad (5)$$

Subtracting E_2 from E_1 gives the cell potential⁴, X :

$$X = E_1 - E_2 \quad (6)$$

Substituting the values for E_1 and E_2 in (6) gives:

$$X = E_1^\circ - E_2^\circ - \frac{rt}{NF} \ln \frac{[A^+][B^-]}{[AB]} + \eta_1 + \eta_2 \quad (7)$$

Since the first three terms are constants they are combined into the single constant, c :

$$X = c + \eta_1 + \eta_2 \quad (8)$$

Expanding η_1 and η_2 by the Tafel equation and regrouping gives:

$$X = c + (a_1 + a_2) + (b_1 + b_2) \ln J \quad (9)$$

Combining the constants of (9) gives:

$$X = C + D \ln J \quad (10)$$

Solving equation (10) for J, the corrosion current density, gives equation (2):

$$J = e^{(X-C)/D} \quad (2)$$

The parameters C and D may be conveniently evaluated in the majority of cases from a simple voltage (X)-current density (J) or modified Tafel plot.

¹ "Electrochemistry," Edmund C. Potter, Cleaver-Hume Press Ltd., London, Page 128 (1956).

² "Interpreting Liquid Ammonia Chemistry with Thermodynamics," William L. Jolly, J. Chem. Ed., 33, 10, Page 513, (1956).

³ "Standard Electrode Potential and Decomposition Voltage of Solutions in Liquid Ammonia," V. Pleskov, Acta Phys Chim 20, Page 583, (1945)

⁴ E. C. Potter, ibid., Page 152.

Definition of Terms

E_1 = The potential of the anode in a battery and consequently the driving force behind local action or decomposition of the solvent at this electrode.

E_2 = The potential of the cathode in a battery and the driving force of cathode local action.

$X = E_1 + E_2$ or the cell potential.

J = The corrosion current density to distinguish this from the previously assigned I , stoichiometric current.*

r = The universal gas constant chosen to distinguish this from the previously assigned R , electrolyte specific resistance.*

t = Absolute temperature chosen to distinguish this from the previously assigned T , discharge time.*

F = Faraday's constant.

$[AB] = 1$, the hypothetical one molar standard state. An example is cited in footnote 4, page 90.

$[A^+]$ = The activity of the cationic autoionization product.

$[B^-]$ = The activity of the anionic autoionization constant.

$[A^+][B^-]/[AB]$ = Autoionization equilibrium constant.

η_1 & η_2 = Overvoltage, (1) anodic, (2) cathodic, local action driving force-natural log base.

$$c = E_1^\circ - E_2^\circ - \frac{rt}{NF} \ln \frac{[A^+][B^-]}{[AB]}$$

a_1 & a_2 = Tafel constants in the original connotation - natural log base.

b_1 & b_2 = Tafel slopes in the original connotation - natural log base.

$C = c + (a_1 + a_2)$, Modified Tafel constant.

$D = (b_1 + b_2)$, Modified Tafel slope.

e = Base of natural logarithms.

*See Page 11.

APPENDIX III

Abstract No. 39 taken from Extended Abstracts,
Electrochemical Society, Fall Meeting, September, 1962

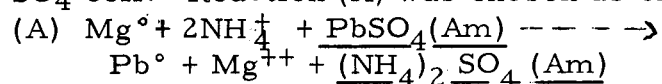
AN APPLICATION OF THERMODYNAMIC METHODS TO THE
DETERMINATION OF REACTIONS AND VOLTAGES IN LIQUID
AMMONIA ELECTROMOTIVE CELLS

by

William F. Meyers
G. & W. H. Corson, Inc.
Plymouth Meeting
Pennsylvania

A semi-empirical method for estimating the potentials of reactions in liquid ammonia electromotive cells is proposed. This method is applied to ten magnesium/heavy metal sulfate couples resulting in a correlation to within 0.06 volts average deviation, based on observed data.

The method is briefly illustrated for the $\text{Mg}/\text{NH}_4\text{SCN}$ in NH_3 (l)/ PbSO_4 cell. Reaction (A) was chosen as characteristic for this type of cell.



Publications of Latimer and Jolly provide tabulations covering standard free energies of all factors excepting the ammoniation, (Am), term for reaction A as well as very numerous other reactions which might be predicated.

Jolly has improved his first method for estimating thermodynamic functions of species in liquid ammonia, after Bjerrum, by accounting for the difference in coordination energy:

$$(1) \quad \Delta F_f^\circ \text{NH}_3 = \Delta F_f^\circ \text{H}_2\text{O} + 16Z + \Delta F_t^\circ$$

Where $\Delta F_f^\circ \text{NH}_3$ is the standard free energy of formation of a species in liquid ammonia, $\Delta F_f^\circ \text{H}_2\text{O}$ is the standard free energy of formation of a species in water, Z is the signed charge of the species, and ΔF_t° represents the difference in affinity of the species for the two ligands NH_3 and H_2O .

The order of procedure is herein reversed and equation (1) is used to evaluate ΔF_t° from the wealth of conveniently tabulated free energy data for unsolvated, aqueous, and ammonia species. To complete a free energy balance over reaction (A) the numerical values for Pb^{++} are substituted into equation (1) giving (2).

$$(2) \quad \Delta F_t^\circ (\text{Pb}^{++}) = 13 - (-5.8) - 16(+2) = -13.2 \text{ kcal/mol}$$

The aqueous species was used as the starting point to allow for the relative nature of the ΔF_t° term and this also accounted for solvent required on the opposite side of the equation since only the affinity of the species for the ligand remains in the calculations. Equilibrium between the solid, and the saturated solution allows the evaluation of $\Delta F_f^\circ \text{NH}_3$ from soluble species in water. Only the cation was considered solvated.

Having evaluated $\Delta F_t^\circ (\text{Pb}^{++})$, this term was added to the standard free energy for crystalline PbSO_4 to account for the (Am) term of reaction (A). Ammonium sulfate (Am) was similarly treated leading to the free energy balance, equation (3), based upon reaction (A).

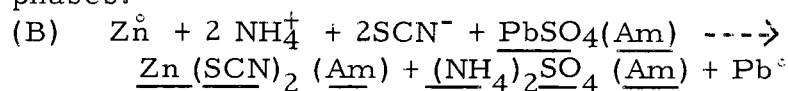
$$\begin{aligned} (3) \quad \Delta Fr + 2(-2.7) + (-193.9 - 13.2) &= \\ &= 0 - 80.4 + (-215-0) \\ \Delta Fr &= -82.9 \text{ kcal} \end{aligned}$$

Since two, N, faradays per mol of lead sulfate are approached in practice, the potential of the $\text{Mg}/\text{NH}_4\text{SCN}$ in NH_3 (1)/ PbSO_4 cell may be estimated:

$$\begin{aligned} (4) \quad E &= -\Delta Fr/NF \\ &= -(-82.9) / 2 \times 23.06 \\ &= 1.80 \text{ Volts} \end{aligned}$$

This compares rather well to our observed value of 1.82 ± 0.03 volts.

Among ten initial comparisons, the cell $\text{Zn}/\text{NH}_4\text{SCN}/\text{PbSO}_4$ was noticeably irregular, to the extent of 0.22 volts from the observed value. However, the reaction chosen, (B), allows the existence of three solid phases.



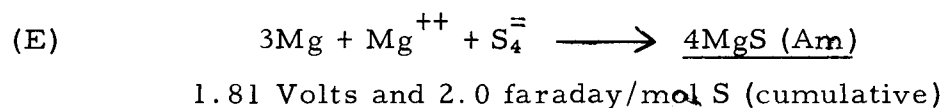
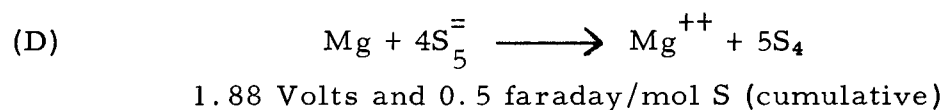
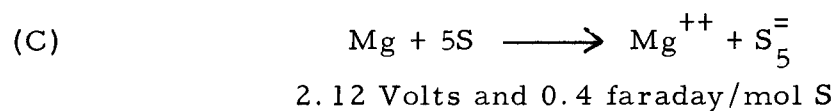
Compensation for this solid anode reaction product, $\text{Zn}(\text{SCN})_2(\text{Am})$, reduces the difference between estimated and observed cell voltages to within 0.02 volts.

In Table I, three different cell types are listed. For entry number 1, the simplest reaction gave reasonable correlation. For entry number 2, it was necessary to take into account the unionized nature of Pb^{++} in solution in ammonia. The use of conductivity ratio for activity ratio appears reasonable and gave good correlation. Entry 3 provided the opportunity for solubility correction in the cathode region and comparison to observed values.

Table I

Ammonia Electromotive Cell	Voltage	
	Observed	Calculated
1. $\text{Mg}/\text{KSCN}/\text{AgCl}$	2.3	2.26
2. $\text{Pb}/\text{NH}_4\text{SCN}/\text{PbO}_2$	1.1	1.12
3. $\text{Mg}/\text{NH}_4\text{SCN}/\text{MnO}_2$	2.58	2.55

An inquiry into the observed performance of the sulfur cathode in ammonia led to the following stepwise reactions using a magnesium anode.



In four different supporting electrolytes reaction (C) is well defined by a potential plateau ranging from 2.12 to 2.18 volts. The potential indicated for reaction (D), being relatively short, is observed as a transition as in aqueous polysulfide potentials. The third plateau is distinctly present in the observed data without supporting electrolyte but approaches the full theoretical capacity in a simple manner only in the acid supporting electrolyte. The presence of more complex polysulfides is indicated from 0.5 to 2.0 faradays per mol of sulfur with K^+ and Mg^{++} supporting electrolytes where the work of Watt and Otto is referenced.

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10 West 35th Street
Chicago 16, Illinois
Attn: Dr. H. T. Francis

Arthur D. Little, Inc.
Cambridge, Massachusetts
Attn: J. H. B. George

Atomics International Division
North American Aviation, Inc.
Canoga Park, California
Attn: Dr. H. L. Recht

Westinghouse Electric Corporation
Research & Development Center
Churchill Borough
Pittsburgh, Pennsylvania
Attn: Dr. S. Barnardt

Yardney Electric Corporation
40-50 Leonard Street
New York 13, New York
Attn: Dr. P. L. Howard

Research Office
R & D Directorate
Army Weapons Command
Rock Island, Illinois
Attn: Mr. G. Reinsmith, Chief

U.S. Naval Ordnance Laboratory
Department of the Navy
Corona, California
Attn: Wm. Spindler

U. S. Army Electronics & Development Lab.
Power Sources Division
Ft. Monmouth, New Jersey 07703
Attn: Mr. Herbert W. Schwartz

I.T.T. Federal Laboratories
500 Washington Avenue
Nutley 10, New Jersey
Attn: Mrs. Dorothy A. Sked

General Electric Company
Research Laboratory
Schenectady, New York
Attn: Dr. Donald Wood

LIVINGSTON ELECTRONIC CORPORATION

Montgomeryville Laboratory

Montgomeryville, Pennsylvania

MANHOURS, COST AND COMMITMENT REPORT FOR PERIOD 8/20/63 to 11/17/63

CONTRACT NO. NAS 3-2775

A. Man Hours Expended

Chief Project Engineer	306.0
Project Engineer	93.0
Design Engineer	640.0
Physicist	251.0
Chemist and X-Ray Analyst	44.5
Junior Engineer	1101.0
Technician	1672.0
Machinist	<u>95.5</u>
Total Hours Expended	<u>4203.0</u>

B. Dollar Expenditures

Engineering Labor - 4203.0 hours (A Above)	\$12,578.16
Engineering Burden at Rate of 50%	<u>6,289.09</u>
	\$18,867.25
Direct Materials	1,020.92
Direct Sub Contracts	106.95
G & A Expenses at Rate of 3.5%	<u>699.83</u>
Total Dollars Expended	<u>\$20,694.95</u>

C. Estimated Commitments

Raw Material	\$ 179.40
Sub Contracts	NONE